Acid Deposition Monitoring Network
in East Asia (EANET)

Report of the Inter-laboratory Comparison Project 2023

26th Inter-laboratory Comparison Project on Wet Deposition

19th Inter-laboratory Comparison Project on Dry Deposition

25th Inter-laboratory Comparison Project on Soil

24th Inter-laboratory Comparison Project on Inland Aquatic Environment

December 2024
Network Center for EANET

Contents

1. INTRODUCTION

The Inter-laboratory Comparison Project was conducted among the analytical laboratories in participating countries of the Acid Deposition Monitoring Network in East Asia (EANET), based on the quality assurance / quality control (QA/QC) programs of EANET.

The objectives of this project are, through the evaluation of analytical results, analytical equipment and its operating condition and other practices;

(i) to recognize the analytical precision and accuracy of the measurement in each participating laboratory;

(ii) to give further opportunities to improve the quality of the analysis on wet deposition, dry deposition (filter pack method), soil and inland aquatic monitoring of EANET;

(iii) to improve reliability of analytical data through the assessment of suitable analytical methods and techniques.

The Inter-laboratory Comparison Project is implemented by the Network Center (NC) of EANET annually for the following items:

a. Wet deposition
b. Dry deposition
c. Soil
d. Inland aquatic environment

This report presented the results of the 26th Inter-laboratory Comparison Project on wet deposition, 19th Inter-laboratory Comparison Project on dry deposition, 25th Inter-laboratory Comparison Project on soil, and 24th Inter-laboratory Comparison Project on inland aquatic environment.

The number of participating laboratories from each country by project is shown in Figure 1.1.
Table 1.1 shows the name and code of participating laboratories and data submission status. A check-mark(✔) indicates the analytical results were submitted by individual laboratories. In addition, laboratories in charge of the analysis of each monitoring site in EANET are listed in Table 1.2.

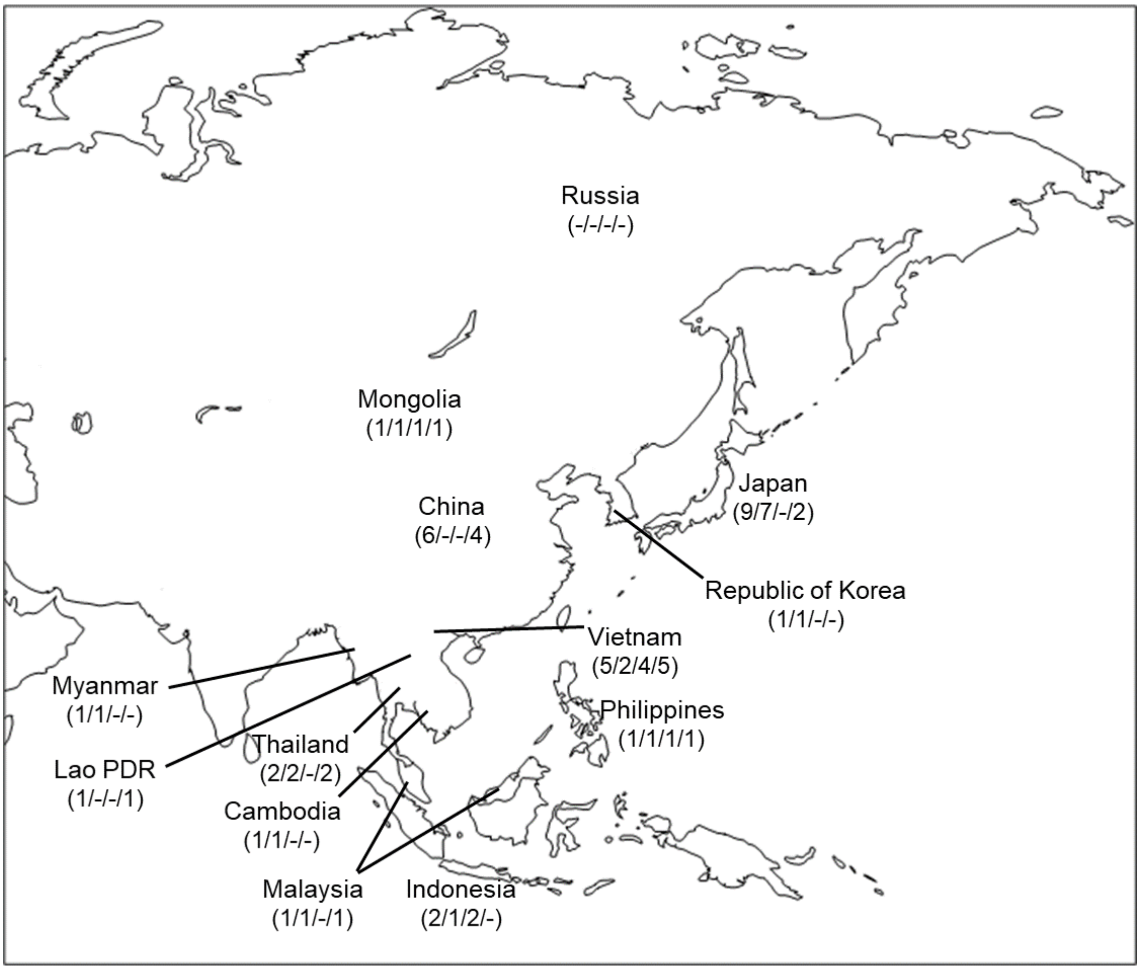


Figure 1.1 Number of participating laboratories in 2023

* The values in parentheses show the number of participating laboratories in each country.

(wet/dry/soil/inland aquatic environment)

Table 1.1 Participating laboratories and data submission status

Participating laboratories	Code	Data submission			
		Wet	Dry	Soil	IAE
Cambodia					
General Directorate of Environmental Protection (GDEP), Ministry of Environment	**KH01**				
China					
Zhuhai Environmental Monitoring Center Station	**CN01**	✔			✔
Xiamen Environmental Monitoring Station	**CN02**	✔			✔
Xi’an Environmental Monitoring Center Station	**CN03**	✔			✔
Chongqing Ecological and Environmental Monitoring Center	**CN04**	✔			✔
Wuzhishan City Ecological Environment Protection Monitoring Station	**CN05**	✔			
The Ecological and Environmental Monitoring Station of DEEY in Lijiang	**CN06**	✔			
Indonesia					
Center for Standardization of Environmental Quality Instrument (PSIKLH)	**ID01**			✔	
Climatology,Meteorological and Geophysical Agency (BMKG)	**ID02**	✔			
Research Organization of Aeronautics and Space - National Research and Innovation Agency (LAPAN-BRIN)	**ID03**	✔	✔		
Indonesian Soil Research Institute (ISRI)	**ID04**			✔	
Japan					
Institute of Environmental Sciences, Hokkaido Research Organization	**JP01**	✔	✔		
Niigata Prefectural Institute of Public Health and Environmental Sciences	**JP02**	✔	✔		
Nagano Environmental Conservation Research Institute	**JP03**	✔	✔		✔
Gifu Prefectural Research Institute for Health and Environmental Sciences	**JP04**	✔	✔		✔
Kochi Prefectural Institute of Health and Environment	**JP07**	✔			
Okinawa Prefectural Institute of Health and Environment	**JP08**	✔	✔		
Asia Center for Air Pollution Research (ACAP)	**JP09**	✔	✔		
Japan Environmental Sanitation Center (JESC)	**JP10**	✔	✔		
Nagasaki Prefectural Institute of Environment and Public Health	**JP14**	✔			
Lao PDR					
Environmental Laboratory (EL), Natural Resource and Environment Research Institute (NRERI), Ministry of Natural Resource and Environment (MoNRE)	**LA01**	✔			✔
Malaysia					
Environmental Quality Division, Department of Chemistry Malaysia (DOC)	**MY01**	✔	✔		✔
Mongolia					
Central Laboratory of Environment and Metrology (CLEM)	**MN01**	✔	✔	✔	✔
Myanmar					
Department of Meteorology and Hydrology (DMH)	**MM01**	✔	✔		
Philippines					
Environmental Management Bureau - Central Office (EMB-CO)	**PH01**	✔	✔	✔	✔
Environmental Management Bureau - Cordillera Administrative Region (EMB-CAR)	**PH02**				
Republic of Korea					
Aerosol research Lab. in National Institute of Environment Research	**KR01**	✔	✔		
Russia					
Limnological Institute, Russian Academy of Sciences, Siberian Branch (LI/RAS/SB)	**RU01**				
Primorsky Center for Environmental Monitoring, Roshydromet (PCEM)	**RU02**				
Thailand					
Pollution Control Department (PCD), Ministry of Natural Resources and Environment (MONRE)	**TH01**	✔	✔		✔
Environmental Research and Training Center (ERTC), Department of Environmental Quality Promotion	**TH02**	✔	✔		✔
Vietnam					
Environmental Laboratory - Center for Environmental Research - Vietnam Institute of Meteorology, Hydrology and Environment (IMHEN)- MoNRE	**VN01**	✔	✔	✔	✔
Mid- Central Regional Hydro Meteorological Center, National Hydro-Meteorological Service of Vietnam (NHMS), MoNRE	**VN02**	✔		✔	✔
Sub-Institute of HydroMeteorology and Climate Change(SIHYMECC)	**VN03**	✔	✔		✔
Center for Hydro-Meteorological and Environmental Networks, National Hydro-Meteorological Service of Vietnam (NHMS), MoNRE	**VN04**	✔		✔	✔
Southern Region Hydro-Meteorological Center, National Hydro-Meteorological Service of Vietnam (NHMS), MoNRE	**VN05**	✔		✔	✔
Total number of submitted data :		**30**	**17**	**8**	**17**

Table 1.2 Laboratories in charge of the analysis of each monitoring site in EANET (2023)

Country	Site for deposition monitoring	Code	Plot for soil and vegetation monitoring	Code	Site for monitoring on inland aquatic environment	Code	Laboratory code			
							Wet	Dry (FP*)	Soil	IAE
Cambodia	Phnom Penh	*KHA001*					KH01	KH01		
					Sras Srang Lake	*KHI002*				KH01
China	Chingqing - Haifu	*CNA003*					CN04			
	- Jinyunshan	*CNA004*	Jinyunshan	*CNS004*	Jinyunshan Lake	*CNI004*	CN04		CN04	CN04
	Xi'an - Shizhan	*CNA005*					CN03			
	- Jiwozi	*CNA007*	Dabagou	*CNS007*	Jiwozi River	*CNI007*	CN03		CN03	CN03
	Xiamen - Hogwen	*CNA008*					CN02	CN02		
	- Xiaoping	*CNA009*	Xiaoping	*CNS009*	Xiaoping Dam	*CNI209*	CN02		CN02	CN02
	Zhuhai - Xiang Zhou	*CNA010*					CN01			
	- Zhuxiandong	*CNA011*	Zhuxiandong	*CNS011*	Zhuxiandong Stream	*CNI111*	CN01		CN01	CN01
	- Haibin-Park	*CNA012*								
	Wuzhishan	*CNA013*					CN05			
	Lijiang	*CNA014*					CN06			
Indonesia	Jakarta	*IDA001*					ID02	ID02		
	Serpong	*IDA002*	Bogor Research Forest	*IDS002*			ID01	ID01	ID01	
	Kototabang	*IDA003*					ID02			
	Bandung	*IDA004*			Patengang Lake	*IDI004*	ID03	ID03		ID01
	Maros	*IDA005*					ID02			
					Gunung Lake	*IDI006*				ID01
	Jembrana	*IDA006*					ID02			
	Lombok	*IDA007*					ID02			
Japan	Rishiri	*JPA001*					JP01	JP01		
	Ochiishi	*JPA002*					JP09	JP09		
	Sado-seki	*JPA004*					JP09	JP02		
	Happo	*JPA005*	Sekido-san	*JPS005*	Futago-ike Lake	*IPI005*	JP03	JP03	JP13	JP03
			Horyu-zan	*JPS105*					JP13	
	Ijira	*JPA006*	Ijira	*JPS006*	Ijira Lake	*JPI006*	JP04	JP04	JP04	JP04
			Yamato	*JPS106*					JP04	
	Oki	*JPA007*					JP09	JP09		
	Yusuhara	*JPA009*					JP07	JP09		
	Hedo	*JPA010*					JP08	JP08		
	Ogasawara	*JPA011*					JP10	JP10		
	Tokyo	*JPA012*					JP10	JP10		
	Niigata-maki	*JPA013*					JP02			
	Tsushima	*JPA014*					JP14	JP09		
Lao PDR	Vientiane	*LAA001*			Nam Houm Lake	*LAI001*	LA01	LA01		LA01
Malaysia	Petaling Jaya	*MYA001*	Pasoh Reserve Forest 1 / 2	*MYS001/ MYS101*			MY01	MY01		
			Pasoh TEAM Plot 1 / 8	*MYS201/ MYS202*						
	Tanah Rata	*MYA002*						MY01		
	Danum Valley	*MYA003*			Baru River	*MYI103*	MY01	MY01		MY01
	Kuching	*MYA004*					MY01			
	Gunung Brinchang	*MYA005*					MY01			
			UPMKB Rehabilitated Forest Planted in 1991 / 2008	*MYS005/ MYS105*						
					Kuala Tahan	*MYI006*				MY01
Mongolia	Ulaanbaatar	*MNA001*	Bogdkhan Mountain	*MNS001*			MN01	MN01	MN01	
	Terelj	*MNA002*	Terelj Mountain	*MNS002*	Terelj River	*MNI002*	MN01	MN01	MN01	MN01
Myanmar	Yangon	*MMA001*					MM01	MM01		
	Mandalay	*MMA002*								
Philippines	Manila Observatory	*PHA001*	La Mesa Wastershed	*PHS001*			PH01	PH01		
	Los Baños	*PHA002*	Mt. Makiling	*PHS002*	Pandin Lake	*PHI102*	PH01	PH01		PH01
			UP Quezon, Land Grant	*PHS102*						
	Mt. Sto. Tomas	*PHA003*	Boneco Long Term Ecological	*PHS003*	Ambulalakaw River	*PHI003*	PH02	PH02		PH02
Republic of Korea	Kanghwa						KR01	KR01		
	Cheju (Kosan)						KR01	KR01		
	Imsil	*KRA003*	Mt. Naejang	*KRS003*			KR01	KR01	KR01	
Russia	Mondy	*RUA001*	Ilchir Lake	*RUS001*			RU01	RU01	RU01	
			Okinskoe Lake	*RUS101*					RU01	
			Solar Observatory	*RUS201*					RU01	
	Listvyanka	*RUA002*	Bolshie Koty	*RUS002*	Pereemnaya River	*RUI102*	RU01	RU01	RU01	RU01
			Pereemnaya river Catchment	*RUS102*					RU01	
	Irkutsk	*RUA003*	Irkutsk	*RUS003*			RU01	RU01	RU01	
	Primorskaya	*RUA004*	Primorskaya	*RUS004*	Komarovka River	*RUI004*	RU02	RU01	RU01	RU02
Thailand	Bangkok	*THA001*					TH01	TH01		
	Samutprakarn	*THA002*					TH01			
	Pathumthani	*THA003*					TH02	TH02		
	Khanchanaburi	*THA004*	Vachiralongkorn Dam	*THS004*	Vachiralongkorn Dam	*THI004*	TH01	TH01		TH01
			Vachiralongkorn Puye	*THS104*						
Vietnam	Hanoi	*VNA001*					VN01	VN01		
	Hoa Binh	*VNA002*	Cave of Heaven	*VNS002*	Hoa Binh Reservoir	*VNI002*	VN01	VN01	VN01	VN01
			Thang Ranh	*VNS102*					VN01	
	Cuc Phuong	*VNA003*					VN04			
	Da Nang	*VNA004*					VN02			
	Can Tho	*VNA005*					VN03	VN03		
	Ho Chi Minh	*VNA006*					VN03	VN03		
	Yen Bai	*VNA007*					VN01	VN01		

* FP: Filter pack method

2. 26th INTER-LABORATORY COMPARISON PROJECT ON WET DEPOSITION

2.1 Introduction

In the 26th Inter-laboratory Comparison Project on wet deposition, artificial rainwater samples containing known amounts of major ions were prepared and distributed to the participating countries of EANET by the Network Center (NC). The measured values of pH, electric conductivity (EC) and concentrations of major ions submitted by the participating countries were compared with the prepared values and were treated statistically.

The NC shipped the artificial rainwater samples to laboratories in charge of chemical analysis in EANET in the middle of October 2023. Their analytical results were required to be submitted to the NC by 28 February 2024.

2.2 Procedures

2.2.1 Participating laboratories

The NC distributed the artificial rainwater samples to 34 laboratories in charge of chemical analysis in 13 countries of EANET. 30 of the participating laboratories submitted their analytical results to the NC. All participating laboratories and their codes and data submission status are listed in Table 1.1 of Chapter 1.

2.2.2 Description of samples

Two kinds of artificial rainwater samples were distributed to the laboratories. A description of the samples is given in Table 2.1.

Table 2.1 Description of artificial rainwater samples

Artificial rain-water sample	Quantity of sample	Container	Number of samples	Note
No. 231w No. 232w	100 mL each	Polypropylene bottle 100 mL	One bottle each	- Fixed quantity of reagents are dissolved in pure water (EC < 0.15 mS m^{-1}) - Ions other than shown in Table 2.2 are not added

The prepared values of analytical parameters in the artificial rainwater samples are described in Table 2.2. These parameters are calculated based on the quantity of reagents.

Table 2.2 Prepared values/concentrations of analytical parameters*

	pH -	EC mS m^{-1}	SO_4^{2-} μmol L^{-1}	NO_3^- μmol L^{-1}	Cl^- μmol L^{-1}	NH_4^+ μmol L^{-1}	Na^+ μmol L^{-1}	K^+ μmol L^{-1}	Ca^{2+} μmol L^{-1}	Mg^{2+} μmol L^{-1}
No. 231w	4.77	2.49	34.1	31.1	47.1	33.3	41.1	4.5	17.4	7.8
No. 232w	5.22	1.02	13.2	14.1	21.8	13.6	18.8	1.8	6.4	4.7

* For 100 times diluted samples.

2.2.3 Analytical methods and data checking procedures

Before the measurement, the samples must be diluted 100 times accurately with pure water (EC < 0.15 mS m^{-1}) in each laboratory according to the specified procedure.

All participating laboratories were expected to analyze the diluted samples for the following 10 parameters: pH, EC, concentrations of SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Na^+, K^+, Ca^{2+} and Mg^{2+}.

The laboratories were required to apply the analytical methods and data checking procedures that were recommended in *Technical Manual for Wet Deposition Monitoring in East Asia -2010*. Analytical methods recommended in the Technical Manual are listed in Table 2.3.

Table 2.3 Analytical methods recommended in the Technical Manual

Parameter	Analytical method
pH	Glass Electrode Method (preferably with the Electrode of non-leak inner cell)
EC	Conductivity Cell Method
SO_4^{2-} NO_3^- Cl^-	Ion Chromatography (preferably with suppressor) Spectrophotometry
NH_4^+	Ion Chromatography Spectrophotometry (Indophenol Blue Method)
Na^+ K^+ Ca^{2+} Mg^{2+}	Ion Chromatography Atomic Absorption Spectrometry Atomic Emission Spectrometry

Checking analytical results was performed using the calculation of ion balance (R_1) and total electric conductivity agreement (R_2).

Calculation of ion balance (R_1)

(1) Total anion equivalent concentration (**A** [μeq L^{-1}]) was calculated by summing the concentrations of all anions (c [μmol L^{-1}]).

$$\mathbf{A}\ [\mu eq\ L^{-1}] = \sum n\ c_{Ai}\ [\mu mol\ L^{-1}] = 2c\ (SO_4^{2-}) + c\ (NO_3^-) + c\ (Cl^-)$$

n, c_{Ai} : electric charge and concentration [μmol L^{-1}] of anion “i”.

(2) Total cation equivalent concentration (**C** [μeq L^{-1}]) was calculated by summing the concentrations of all cations (c [μmol L^{-1}]).

$$\mathbf{C}\ [\mu eq\ L^{-1}] = \sum n\ c_{Ci}\ [\mu mol\ L^{-1}] = 10^{(6\text{-}pH)} + c\ (NH_4^+) + c\ (Na^+) + c\ (K^+) + 2c\ (Ca^{2+}) + 2c\ (Mg^{2+})$$

n, c_{Ci} : electric charge and concentration [μmol L^{-1}] of cation “i”.

(3) Calculation of ion balance (R_1)

$$R_1 = 100 \times (\mathbf{C}-\mathbf{A}) / (\mathbf{C}+\mathbf{A})$$

(4) R_1 calculated by the above equation was compared with allowable ranges specified in *Technical Manual for Wet Deposition Monitoring in East Asia -2010* which are shown in Table 2.4. If R_1 was out of the range, re-measurement, check with standard solutions, and/or inspection of calibration curves were required.

Table 2.4 Allowable ranges for R_1 in different concentration ranges

C+A [μeq L^{-1}]	R_1 [%]
< 50	± 30
50 – 100	± 15
> 100	± 8

Comparison between calculated and measured values of electrical conductivity (R_2)

(1) Total electrical conductivity (Λ calc) was calculated as follows;

$$\Lambda \text{ calc } [\text{mS m}^{-1}] = \{349.7 \times 10^{(6\text{-pH})} + 80.0 \times 2c\,(SO_4^{2-}) + 71.4 \times c\,(NO_3^-) + 76.3 \times c\,(Cl^-) + 73.5 \times c\,(NH_4^+) + 50.1 \times c\,(Na^+) + 73.5 \times c\,(K^+) + 59.5 \times 2c\,(Ca^{2+}) + 53.0 \times 2c\,(Mg^{2+})\} / 10000$$

c : Molar concentrations [μmol L^{-1}] of ions in the parenthesis; each constant value was ionic equivalent conductance at 25 degrees centigrade.

(2) Electrical conductivity comparison (R_2) was calculated as follows;

$$R_2 = 100 \times (\Lambda \text{ calc} - \Lambda \text{ meas})/(\Lambda \text{ calc} + \Lambda \text{ meas})$$

Λ meas : measured conductivity

(3) R_2 calculated by the above equation was compared with allowable ranges specified in the Technical Manual which are shown in Table 2.5. If R_2 was out of the range, re-measurement, check with standard solutions, and/or inspection of calibration curves were required.

Table 2.5 Allowable ranges for R_2 in different ranges of EC

Λ meas [mS m^{-1}]	R_2 [%]
< 0.5	± 20
0.5 – 3	± 13
> 3	± 9

2.3 Results

The NC received the analytical results from 30 laboratories in the participating countries of EANET.

Basic statistics of submitted data summarized in Table 2.6 was calculated for each parameter of the artificial rainwater samples such as: average (Va), minimum (Min.), maximum (Max.), standard deviation (S.D.), and number of data (N). The outliers, exceeding three standard deviations, were excluded from the calculation. As shown in Table 2.6, the range of ΔV/Vp was between -3.6% to 4.9% for sample No. 231w, and -0.8% to 7.8% for sample No. 232w.

Table 2.6 Summary of analytical results of the artificial rainwater samples (Reported data after removing outliers)

Sample No. 231w

Constituents		Prepared (Vp)	Average (Va)	ΔV/Vp[*1] %	S.D.	N	Min.	Max.
pH		4.77	4.85	1.8	0.16	29	4.42	5.23
EC	[mS m^{-1}]	2.49	2.40	-3.6	0.07	28	2.26	2.55
SO_4^{2-}	[μmol L^{-1}]	34.1	34.0	-0.3	1.19	29	31.6	38.3
NO_3^-	[μmol L^{-1}]	31.1	31.3	0.6	1.25	30	28.7	34.5
Cl^-	[μmol L^{-1}]	47.1	47.0	-0.1	1.19	28	43.3	49.5
NH_4^+	[μmol L^{-1}]	33.3	32.9	-1.1	1.34	29	30.0	35.7
Na^+	[μmol L^{-1}]	41.1	41.1	0.0	1.48	29	37.6	44.4
K^+	[μmol L^{-1}]	4.5	4.4	-2.9	0.32	28	3.4	4.8
Ca^{2+}	[μmol L^{-1}]	17.4	18.3	4.9	2.08	29	14.4	24.2
Mg^{2+}	[μmol L^{-1}]	7.8	7.9	0.8	0.73	29	5.8	9.4

Sample No. 232w

Constituents		Prepared (Vp)	Average (Va)	ΔV/Vp[*1] %	S.D.	N	Min.	Max.
pH		5.22	5.25	0.6	0.09	28	5.11	5.42
EC	[mS m^{-1}]	1.02	1.03	0.7	0.04	28	0.95	1.12
SO_4^{2-}	[μmol L^{-1}]	13.2	13.3	0.5	0.70	29	11.6	15.3
NO_3^-	[μmol L^{-1}]	14.1	14.1	0.2	0.54	29	12.7	15.3
Cl^-	[μmol L^{-1}]	21.8	21.8	0.2	0.98	28	19.5	24.8
NH_4^+	[μmol L^{-1}]	13.6	13.8	1.7	0.93	29	11.6	16.3
Na^+	[μmol L^{-1}]	18.8	18.8	-0.2	1.12	28	16.3	21.2
K^+	[μmol L^{-1}]	1.8	1.8	0.8	0.34	28	0.7	2.6
Ca^{2+}	[μmol L^{-1}]	6.4	6.9	7.8	1.00	29	5.4	9.4
Mg^{2+}	[μmol L^{-1}]	4.7	4.7	-0.8	0.47	29	3.5	6.0

Note: *1, (Va-Vp)/Vp x 100

The Data Quality Objective for accuracy (hereafter referred to as DQO) is specified in the QA/QC program of EANET for every parameter to be within ±15% of deviation* from Vp. In this report, analytical data of the artificial rainwater samples were compared with Vp, and the data exceed DQO were marked with flags. The flag “E” indicates that the deviation from Vp exceeds ±15% but not ±30%, and the flag “X” indicates that the deviation from Vp exceeds ±30%.

*According to *Technical Manual for Wet Deposition Monitoring in East Asia -2010*, deviation is calculated using the following formula:
Deviation = [(analytical values) - Vp] x 100 / Vp

A set of data for each sample was evaluated by the data checking procedures described in section 2.2.3. The flag “I” and the flag “C” were put to the data sets with poor ion balance and poor conductivity agreement, respectively.

The results were evaluated by the following three aspects:

i) Comparison of concentration dependence on level of their concentration
– sample No. 231w and No. 232w,
ii) Comparison of individual parameters,
iii) Comparison of circumstances of chemical analysis in each participating laboratory.

Evaluation of analytical data on both sample No. 231w and No. 232w is presented in 2.3.1 Evaluation of laboratories’ performance (by sample), evaluation of analytical data for each constituent is presented in 2.3.2 Evaluation of laboratories’ performance (by analytical parameter), and evaluation of analytical data by the circumstances of chemical analysis such as analytical method used, experience of personnel in charge, and other analytical condition are presented in 2.3.4 Information on laboratories.

2.3.1 Evaluation of laboratories' performance (by sample)

1) Sample No. 231w

The number and percentage of the flagged data for sample No. 231w are shown in Table 2.7. 14 analytical data out of 292 were flagged by "E". And 2 analytical data out of 292 were flagged by "X". Data flagged by "E" and "X" shared 5.5 percent of all the submitted data for sample No. 231w.

The data normalized by prepared value in each parameter are shown in Figure 2.1.

Table 2.7 Number of flagged data for the Sample No. 231w

Charactarization of data	pH	EC	SO_4^{2-}	NO_3^-	Cl^-	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	Total
Data within DQO	29	28	29	30	29	29	29	26	22	25	276
Data with flag E[*1]	0	0	1	0	0	0	0	3	6	4	14
Data with flag X[*2]	0	1	0	0	0	0	0	0	1	0	2
Flagged data [%]	0.0	3.4	3.3	0.0	0.0	0.0	0.0	10.3	24.1	13.8	5.5

(Total data = 292)

Note: *1, flag E: 15%<| Deviation |≤30% *2, flag X: 30%<| Deviation |

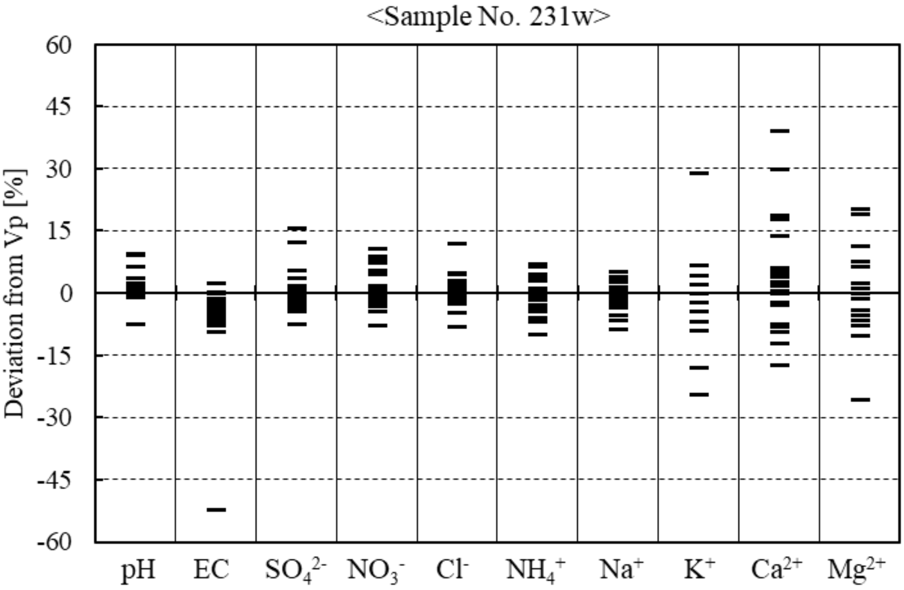


Figure 2.1 Distribution of the data normalized by prepared value in each parameter for sample No. 231w

The parameter which had the most flags was Ca^{2+}. The analytical data submitted by the participating laboratories are shown in Table 2.8 with flags.

Table 2.8 Analytical Results of Sample No. 231w

Lab. ID[*1]	pH	EC mS m^{-1}	SO_4^{2-} µmol L^{-1}	NO_3^- µmol L^{-1}	Cl^- µmol L^{-1}	NH_4^+ µmol L^{-1}	Na^+ µmol L^{-1}	K^+ µmol L^{-1}	Ca^{2+} µmol L^{-1}	Mg^{2+} µmol L^{-1}	R_1 %	R_2 %
KH01[*2]	*(4.13)*	*(2.27)*	*(38.1)*	*(28.6)*	*(41.1)*	*(34.8)*	*(37.3)*	*(3.8) E*	*(16.9)*	*(4.6) X*	*(13.9) I*	*(32.3) C*
CN01	4.77	2.39	33.9	32.5	47.0	32.8	41.4	4.2	17.9	7.4	-0.4	2.2
CN02	4.81	2.45	33.9	30.8	47.0	33.3	40.4	4.4	18.3	7.5	-0.1	-0.2
CN03	4.79	2.45	33.2	30.7	47.3	33.3	41.3	4.4	18.5	7.5	1.0	0.2
CN04	4.82	2.49	34.6	30.6	47.4	32.2	39.7	4.6	18.4	7.8	-1.1	-1.1
CN05	4.82	2.40	34.8	31.3	47.4	33.3	44.4	4.5	17.4	7.9	-0.1	1.3
CN06	4.89	2.40	32.8	30.7	47.5	33.3	39.8	4.1	15.8	7.2	-2.8	-2.2
ID02	4.82	2.35	38.3	33.6	52.8	30.0	42.5	3.7 E	17.0	7.4	-7.5	3.6
ID03	4.81	2.26	39.5 E	33.9	49.5	31.9	42.3	4.1	17.4	7.3	-6.3	6.1
JP01	4.86	2.46	34.0	31.7	46.5	31.9	39.9	4.8	15.3	7.7	-3.5	-2.5
JP02	4.81	2.41	33.9	31.3	47.9	34.6	42.8	4.7	18.4	9.3 E	2.0	1.7
JP03	4.78	2.50	34.5	31.4	47.4	33.4	41.3	4.4	17.5	7.9	-0.4	-0.1
JP04	4.73	2.49	34.3	31.0	46.3	33.6	40.2	4.5	16.9	7.7	0.1	1.0
JP07	4.80	2.55	34.2	30.7	47.1	34.5	40.6	4.1	16.1	7.3	-1.5	-2.3
JP08	4.80	2.39	33.8	31.0	47.5	33.5	41.3	4.5	17.7	7.9	0.1	1.4
JP09	4.85	2.46	34.1	31.1	47.0	33.0	41.5	4.4	17.5	7.8	-0.9	-1.4
JP10	4.80	2.50	34.7	31.1	46.5	32.1	40.9	4.4	18.1	8.0	-0.5	-0.8
JP14	5.08	2.37	36.0	32.8	49.3	32.4	42.7	5.8 E	18.2	7.4	-4.6	-2.2
LA01	---	---	31.6	28.7	43.3	32.8	39.0	4.4	18.2	7.8	---	---
MY01	4.85	2.44	33.6	30.3	46.7	35.5	42.2	4.7	17.5	7.5	0.8	-0.9
MN01	4.42	2.35	34.0	33.4	48.2	34.3	43.2	3.4 E	19.8	8.4	7.9	16.8 C
MM01	4.94	1.19 X	33.4	29.8	47.4	35.7	42.5	4.4	17.8	8.0	0.6	32.1 C
PH01	4.80	2.34	35.4	30.2	46.7	33.7	41.8	4.7	20.5 E	9.4 E	2.7	3.9
KR01	4.85	2.35	32.8	30.1	46.3	32.2	41.2	4.1	16.0	7.0	-1.6	-0.5
TH01	4.76	2.46	32.6	34.5	46.0	---	---	---	---	---	---	---
TH02	4.86	2.37	34.7	31.4	47.6	31.3	42.3	4.5	14.4 E	5.8 E	-5.7	-0.8
VN01	5.22	2.32	33.5	31.1	46.0	31.2	40.1	4.2	20.7 E	8.3	-1.6	-4.6
VN02	5.21	2.31	33.1	31.5	46.7	31.0	40.1	4.3	20.7 E	8.3	-1.7	-4.3
VN03	4.81	2.35	33.3	30.9	---	32.4	38.4	4.8	22.6 E	9.3 E	---	---
VN04	5.23	2.33	33.8	30.6	44.9	31.4	40.0	4.2	20.5 E	8.4	-1.3	-5.1
VN05	4.78	2.30	33.0	30.2	48.6	34.8	37.6	4.8	24.2 X	8.7	4.9	5.2
Vp	4.77	2.49	34.1	31.1	47.1	33.3	41.1	4.5	17.4	7.8	0.0	0.1
N of data	29	29	30	30	29	29	29	29	29	29		
Within DQO	29	28	29	30	29	29	29	26	22	25		
Flag E	0	0	1	0	0	0	0	3	6	4		
Flag X	0	1	0	0	0	0	0	0	1	0		

Note: "E", 15%<| Deviation |≤30% ; "X", 30%<| Deviation |

"I", Poor ion balance (R_1); "C", Poor conductivity agreement (R_2); "---", Not measured; "Vp", Prepared values of parameters;

▨ The outliers judged by 3S.D. method were painted with light mesh and excluded from statistics in Table 2.6.

*1: The abbreviated name and code are given in Chapter 1

*2: Data were treated as reference values in this survey since they had been submitted after disclosure of Vp.

2) Sample No. 232w

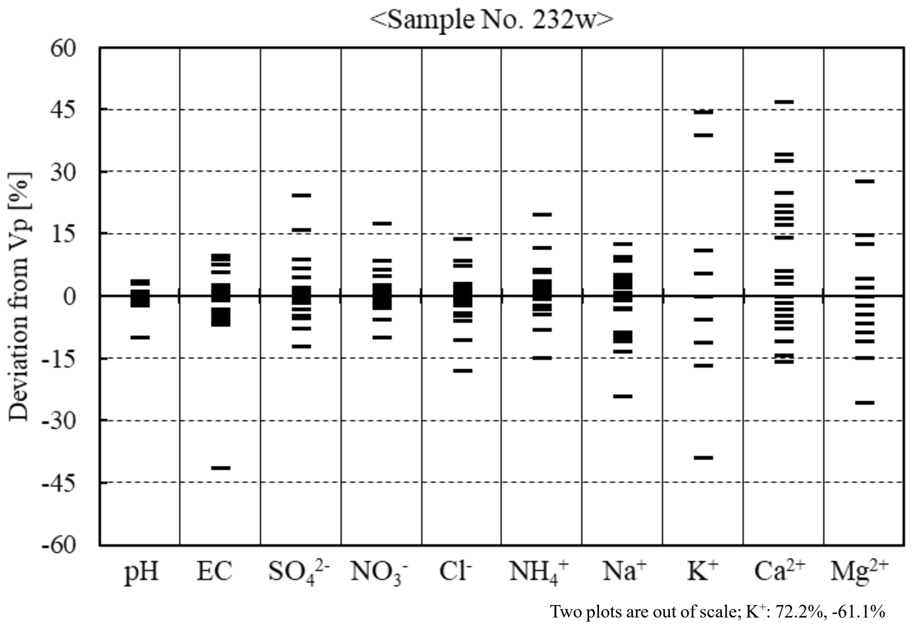
The number and percentage of the flagged data for sample No. 232w are shown in Table 2.9.
19 analytical data out of 292 were flagged by "E". 9 analytical data out of 292 were flagged by "X". Data marked with flags shared up to 9.6 percent of all the submitted data for sample No. 232w.
The normalized data by prepared value in each parameter are shown in Figure 2.2.

Table 2.9 Number of flagged data for the sample No. 232w

Charactarization of data	pH	EC	SO_4^{2-}	NO_3^-	Cl^-	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	Total
Data within DQO	29	28	28	29	28	27	28	23	17	27	264
Data with flag E[*1]	0	0	2	1	1	2	1	1	9	2	19
Data with flag X[*2]	0	1	0	0	0	0	0	5	3	0	9
Flagged data [%]	0.0	3.4	6.7	3.3	3.4	6.9	3.4	20.7	41.4	6.9	9.6

(Total data = 292)

Note: *1, flag E: 15%<| Deviation |≤30% *2, flag X: 30%<| Deviation |



Two plots are out of scale; K^+: 72.2%, -61.1%

Figure 2.2 Distribution of the data normalized by prepared value for each parameter for sample No. 232w

The parameter which had the most flags was Ca^{2+}, which is the same tendency as No.231w. The analytical data submitted by the participating laboratories are shown in Table 2.10 with flags.

Table 2.10 Analytical Results of Sample No. 232w

Lab. ID*1	pH	EC mS m^{-1}	SO_4^{2-} µmol L^{-1}	NO_3^- µmol L^{-1}	Cl^- µmol L^{-1}	NH_4^+ µmol L^{-1}	Na^+ µmol L^{-1}	K^+ µmol L^{-1}	Ca^{2+} µmol L^{-1}	Mg^{2+} µmol L^{-1}	R_1 %	R_2 %
KH01 *2	*(5.05)*	*(0.94)*	*(16.9) E*	*(15.0)*	*(20.9)*	*(11.5) E*	*(14.9) E*	*(0.4) X*	*(6.0)*	*(2.1) X*	*-(14.6) I*	*(8.04)*
CN01	5.20	1.02	13.8	14.5	22.3	14.0	18.9	1.8	7.6 E	4.5	0.6	2.1
CN02	5.23	1.05	14.4	14.1	21.8	13.9	18.7	1.8	7.5 E	4.7	0.0	0.1
CN03	5.38	1.02	14.1	13.7	22.1	14.1	19.6	1.7	7.8 E	4.6	0.3	-1.3
CN04	5.29	1.02	13.2	13.7	21.9	13.6	18.8	2.0	7.7 E	4.5	1.5	-0.8
CN05	5.21	1.00	13.5	14.2	22.0	13.3	18.4	1.8	6.1	4.6	-1.7	1.3
CN06	5.27	1.01	12.5	14.1	22.0	13.7	19.3	1.6	7.3	4.6	2.1	-0.4
ID02	5.19	0.99	16.4 E	16.6 E	24.8	13.0	19.8	1.8	7.6 E	4.9	-5.8	7.3
ID03	5.21	1.10	15.3 E	15.0	21.7	11.6	19.3	1.9	6.8	4.3	-4.8	-2.1
JP01	5.29	1.08	13.2	14.8	22.1	13.7	18.7	2.0	6.0	4.7	-1.9	-4.1
JP02	5.19	1.03	13.4	14.1	21.7	14.5	20.4	1.9	6.6	6.0 E	4.5	2.0
JP03	5.12	1.11	13.5	14.5	22.1	13.9	19.0	1.8	6.3	4.6	0.4	-1.0
JP04	5.16	1.05	13.4	14.2	21.4	13.7	18.3	1.8	6.4	4.7	0.4	0.1
JP07	5.19	1.12	13.1	13.8	21.8	13.8	19.0	1.9	5.9	4.5	0.1	-4.2
JP08	5.20	0.98	13.3	14.1	21.8	13.7	18.9	1.8	6.6	4.8	0.8	2.9
JP09	5.24	1.05	13.3	14.2	21.8	13.7	18.9	1.7	6.4	4.7	-0.3	-1.7
JP10	5.18	1.08	13.4	14.1	21.3	13.2	18.6	1.7	6.7	4.9	0.9	-1.7
JP14	5.42	1.02	14.4	15.3	23.7	13.8	19.4	2.5 X	6.1	4.4	-5.7	-1.5
LA01	---	---	12.2	12.7	19.5	15.2	18.2	1.8	8.0 E	4.8	---	---
MY01	5.28	1.05	12.2	13.3	21.3	16.3 E	19.2	1.7	5.7	4.2	2.7	-3.6
MN01	4.70	1.05	13.2	15.0	22.5	13.5	20.6	1.1 X	8.6 X	5.3	13.0 I	19.4 C
MM01	5.39	0.60 X	13.1	13.8	21.6	16.3 E	21.2	2.0	7.8 E	5.3	6.2	25.2 C
PH01	5.22	0.99	13.0	13.7	23.4	14.1	16.9	0.7 X	8.5 X	5.4	1.9	2.8
KR01	5.24	1.05	12.8	13.8	21.6	14.5	18.7	1.5 E	5.4 E	4.0	-1.5	-3.1
TH01	5.13	1.04	11.6	15.0	20.5	---	---	---	---	---	---	---
TH02	5.22	1.02	13.4	14.0	22.1	13.6	19.5	2.0	5.5	3.5 E	-3.1	-0.6
VN01	5.40	0.96	13.1	13.8	20.9	13.2	17.0	1.9	6.1	4.3	-3.4	-2.1
VN02	5.42	0.95	13.2	13.9	20.8	13.3	16.8	2.0	6.0	4.4	-3.7	-1.8
VN03	5.22	0.96	13.2	14.3	---	12.5	16.3	3.1 X	9.4 X	5.3	---	---
VN04	5.41	0.97	13.2	13.7	20.9	13.0	17.2	2.0	6.2	4.4	-3.1	-2.6
VN05	5.11	0.99	12.6	14.4	17.9 E	14.4	14.3 E	2.6 X	7.5 E	4.3	4.3	2.6
Vp	5.22	1.02	13.2	14.1	21.8	13.6	18.8	1.8	6.4	4.7	0.1	0.1
N of data	29	29	30	30	29	29	29	29	29	29		
Within DQO	29	28	28	29	28	27	28	23	17	27		
Flag E	0	0	2	1	1	2	1	1	9	2		
Flag X	0	1	0	0	0	0	0	5	3	0		

Note: "E", 15%<| Deviation |≤30% ; "X", 30%<| Deviation |

"I", Poor ion balance (R_1); "C", Poor conductivity agreement (R_2); "---", Not measured; "Vp", Prepared values of parameters;

▨ The outliers judged by 3S.D. method were painted with light mesh and excluded from statistics in Table 2.6.

*1: The abbreviated name and code are given in Chapter 1

*2: Data were treated as reference values in the following graphs/tables since they had been submitted after disclosure of Vp.

3) Comparison of high and low concentration sample

The percentage of the flagged data for sample No. 231w and 232w are shown in Figure 2.3. The percentage of the data within the DQO for sample No. 231w and 232w were 94.5% and 90.4%, respectively. The difference between both samples was 4.1%. In this project, the total number of flagged data was 44 (E: 33, X: 11) out of all the 584 data.

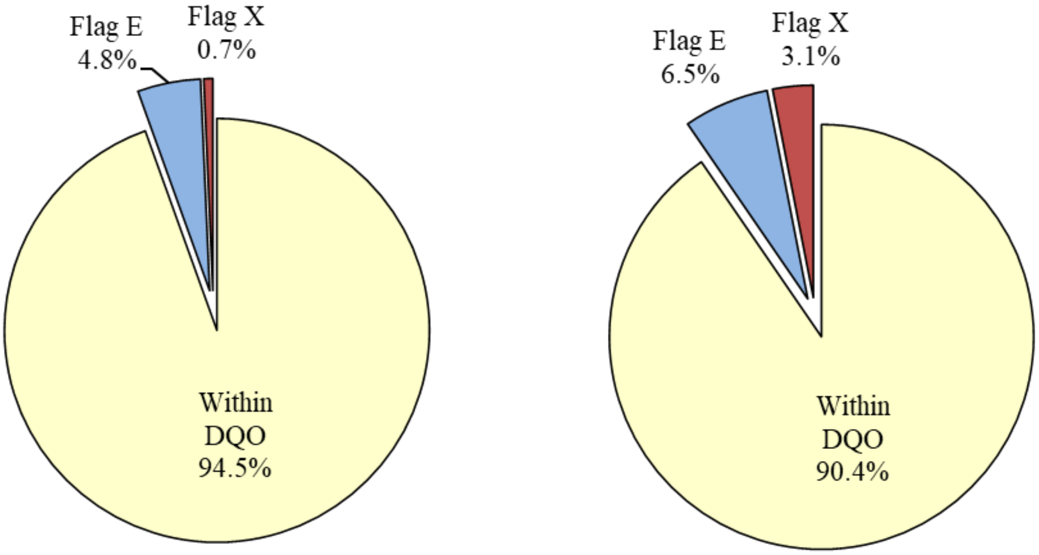


Figure 2.3 Percentage of flagged data for sample No. 231w and No. 232w (Left: No. 231w, Right: No. 232w)

4) The number of laboratory (by number of flags)

The number of laboratories by number of flags is shown in Figure 2.4. The number of laboratories without flagged data was 10, which corresponds to 33.1% of all the participating laboratories.

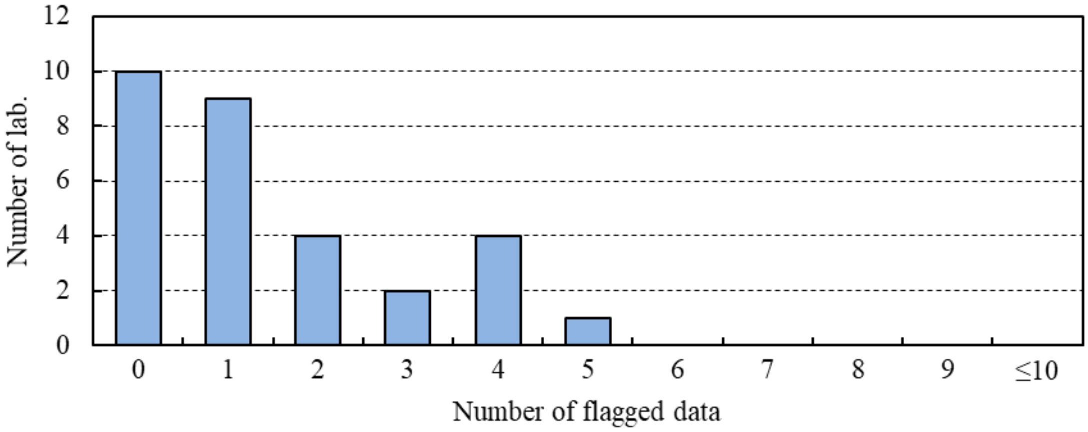


Figure 2.4 Distribution of the number of laboratory (by number of flags)

2.3.2 Evaluation of laboratories’ performance (by analytical parameter)

The data normalized by Vp are shown in Figures 2.5 through 2.24 for each parameter. In scatter diagrams (lower figures), bold line means the prepared values of sample No. 231w and 232w, broken lines and dotted lines showed the values of Vp ± 15% and Vp ± 30%, respectively.

1) pH

All participating laboratories used pH meter with glass electrode method for the measurement of pH. None of the data was marked with flag “E” nor “X”.

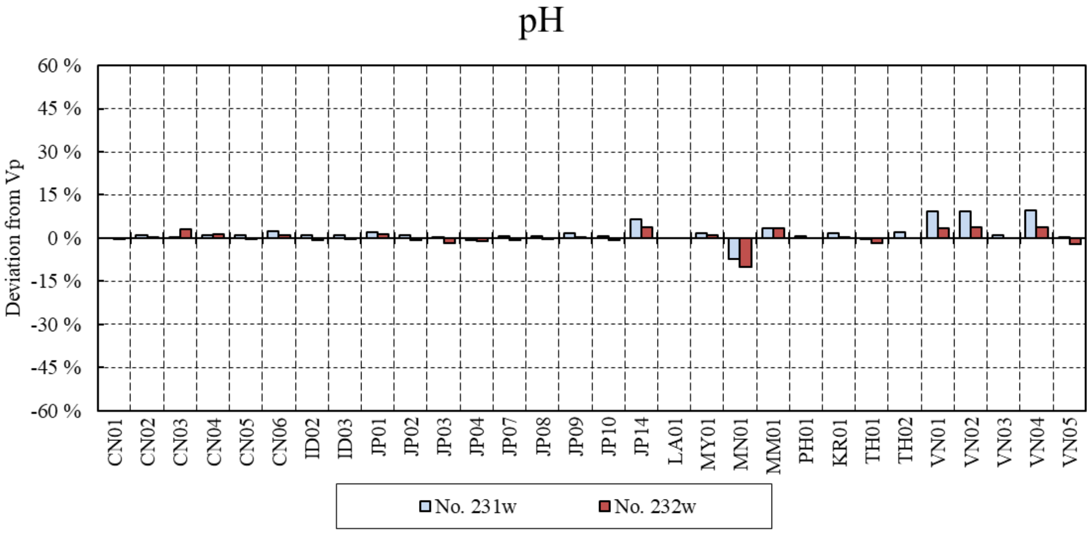


Figure 2.5 Deviation from prepared value for pH (normalized by prepared value)

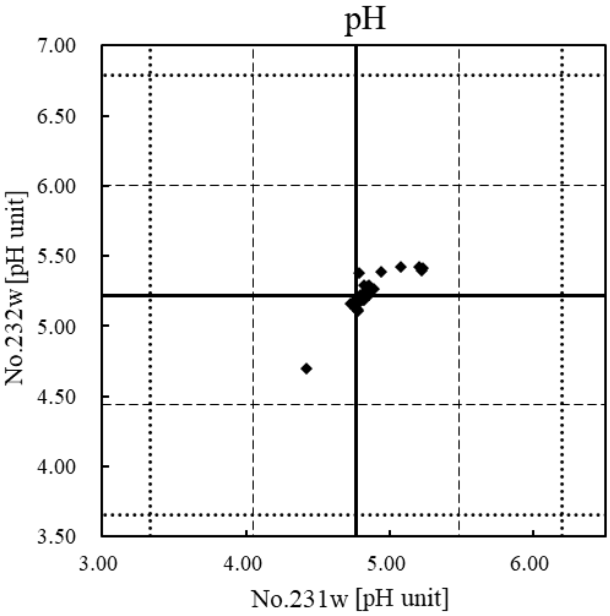


Figure 2.6 Scatter diagram for pH

2) EC

All participating laboratories used conductivity cell method for the measurement of EC. The data of sample No.231 and No.232w from MM01 was marked with flag “X”.

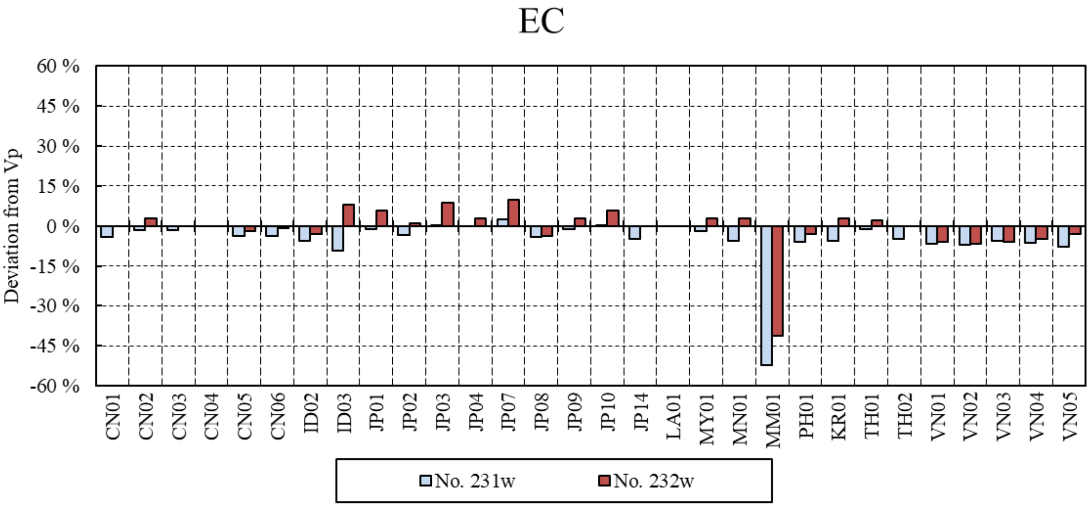


Figure 2.7 Deviation from prepared value for EC (normalized by prepared value)

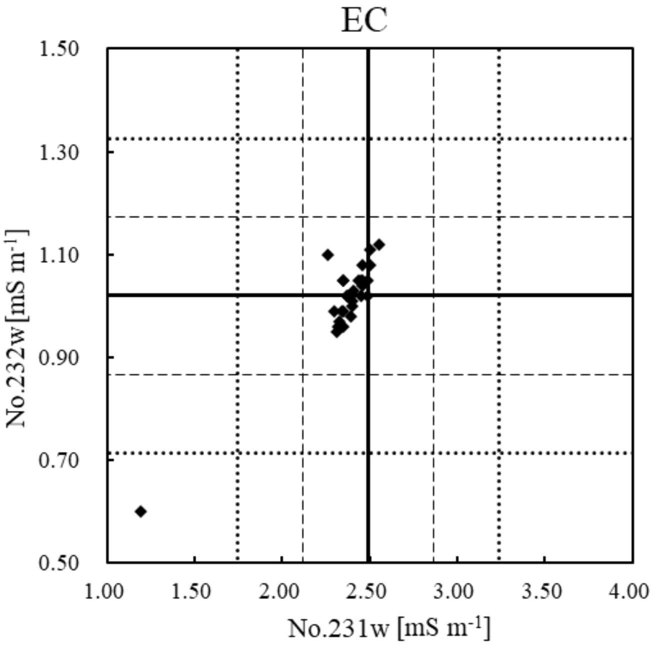


Figure 2.8 Scatter diagram for EC

3) SO_4^{2-}

The data of sample No.231 from ID03 and No.232w from 2 laboratories (ID02 and ID03) were marked with flag “E”.

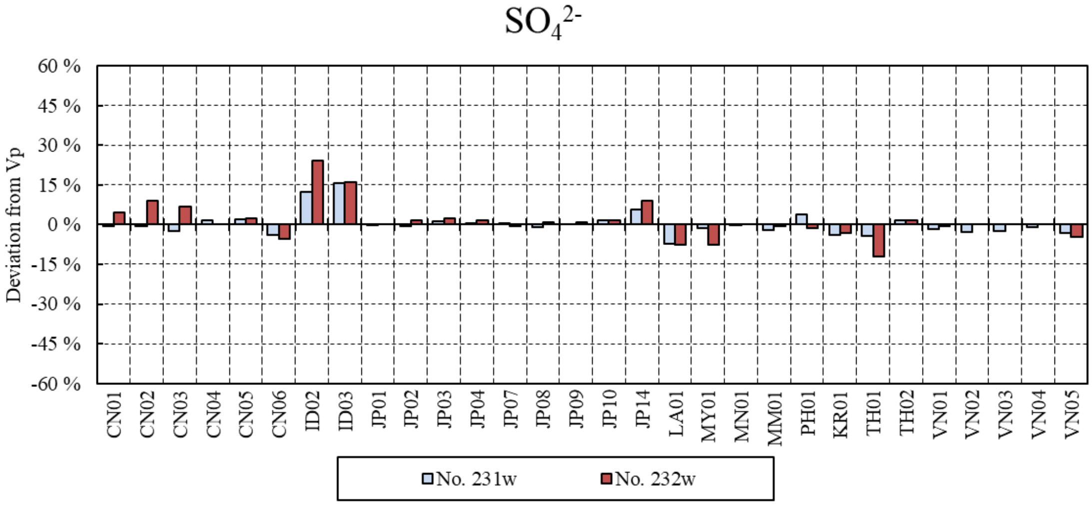


Figure 2.9 Deviation from prepared value for SO_4^{2-} (normalized by prepared value)

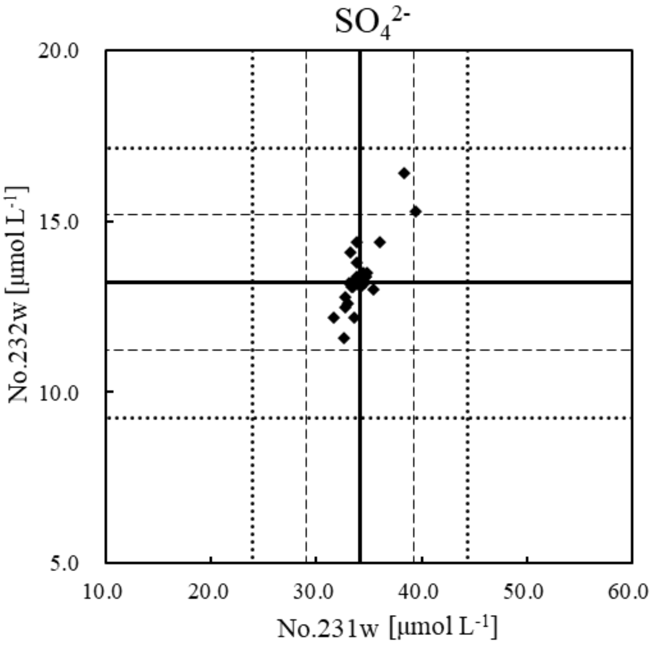


Figure 2.10 Scatter diagram for SO_4^{2-}

4) NO_3^-

The data of sample No.232 from ID02 was marked with flag “E”.

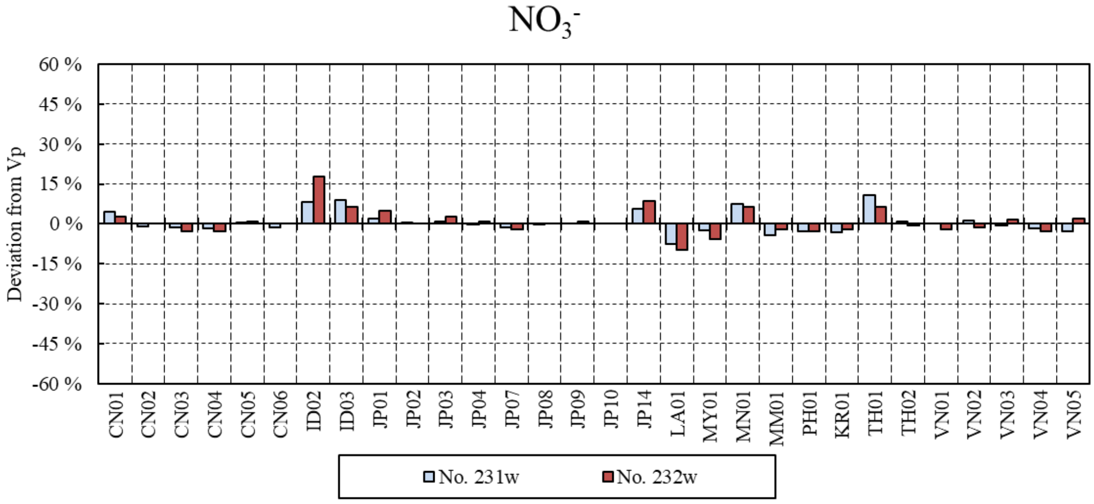


Figure 2.11 Deviation from prepared value for NO_3^- (normalized by prepared value)

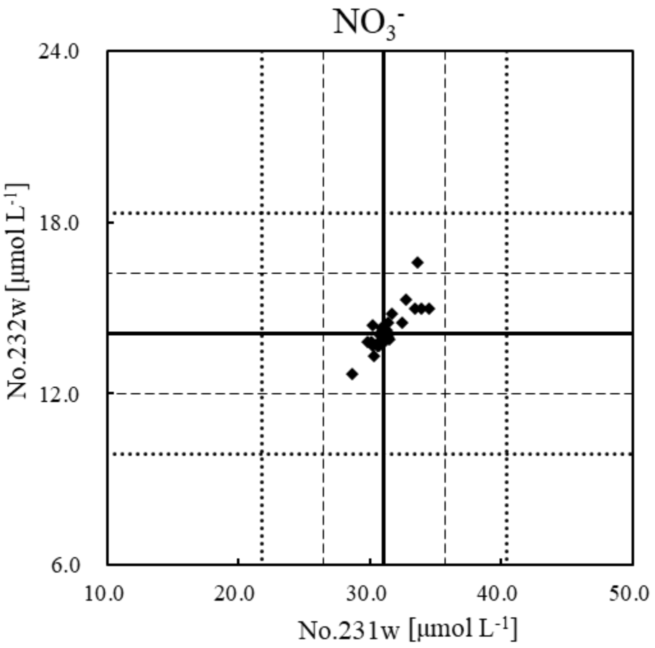


Figure 2.12 Scatter diagram for NO_3^-

5) Cl^-

The data of sample No.232 from VN05 was marked with flag “E”.

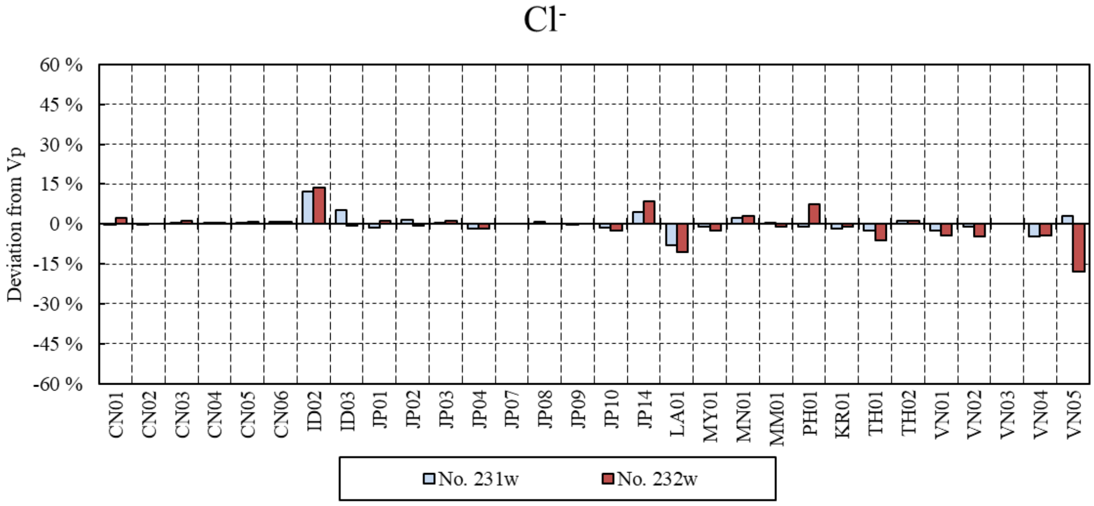


Figure 2.13 Deviation from prepared value for Cl^- (normalized by prepared value)

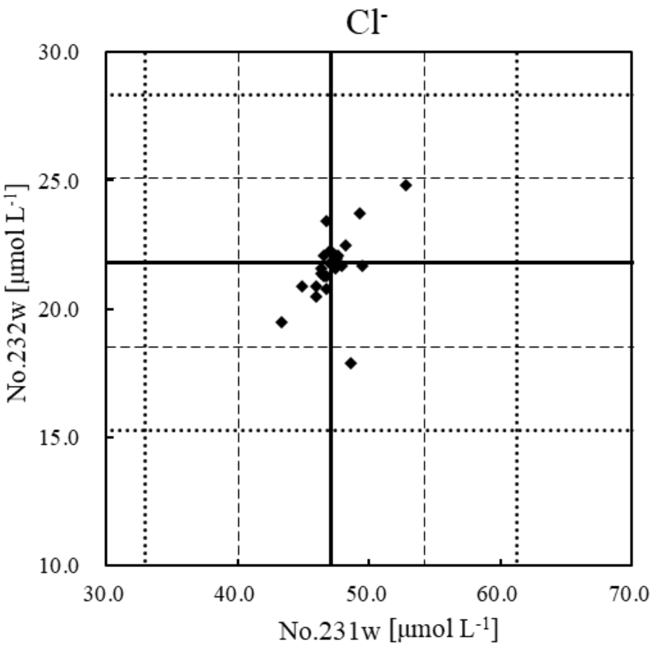


Figure 2.14 Scatter diagram for Cl^-

6) NH_4^+

The data of sample No.232w from 2 laboratories (MY01 and MM01) were marked with flag “E”.

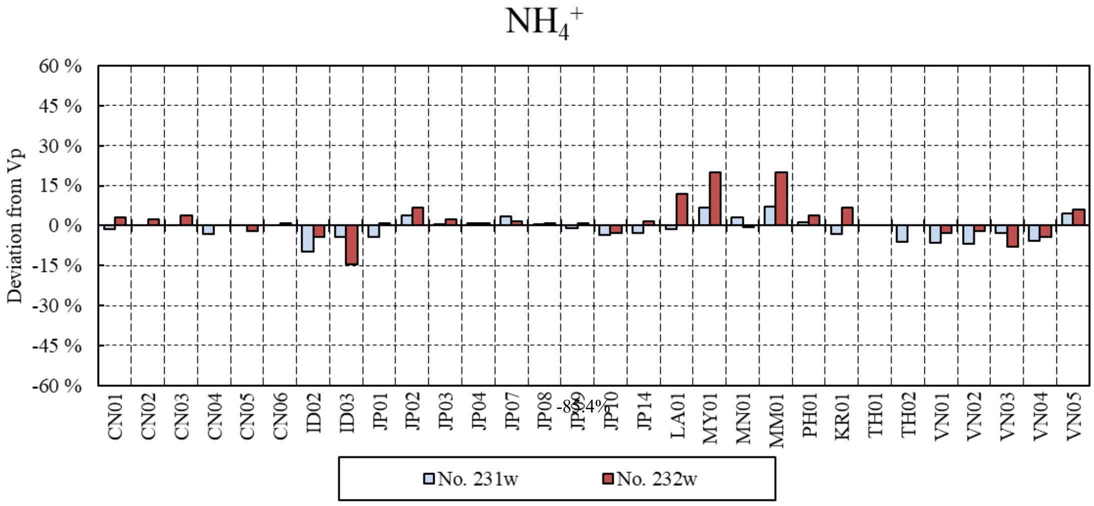


Figure 2.15 Deviation from prepared value for NH_4^+ (normalized by prepared value)

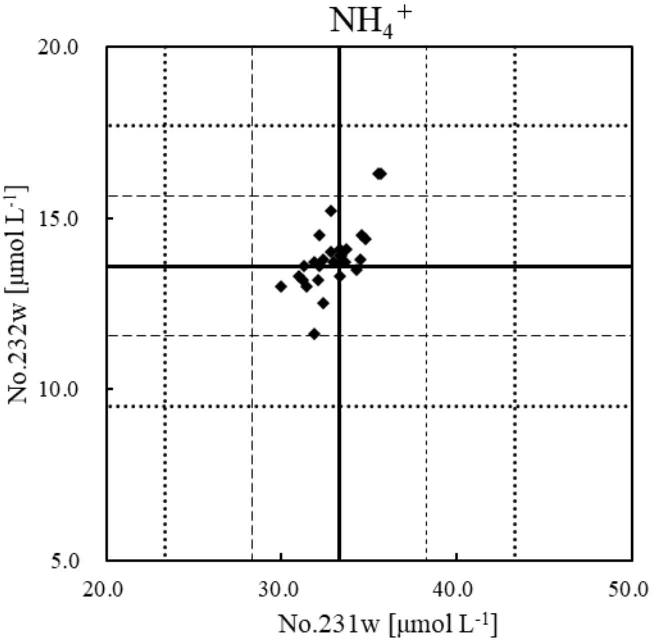


Figure 2.16 Scatter diagram for NH_4^+

7) Na^+

The data of sample No.232 from VN05 was marked with flag “E”.

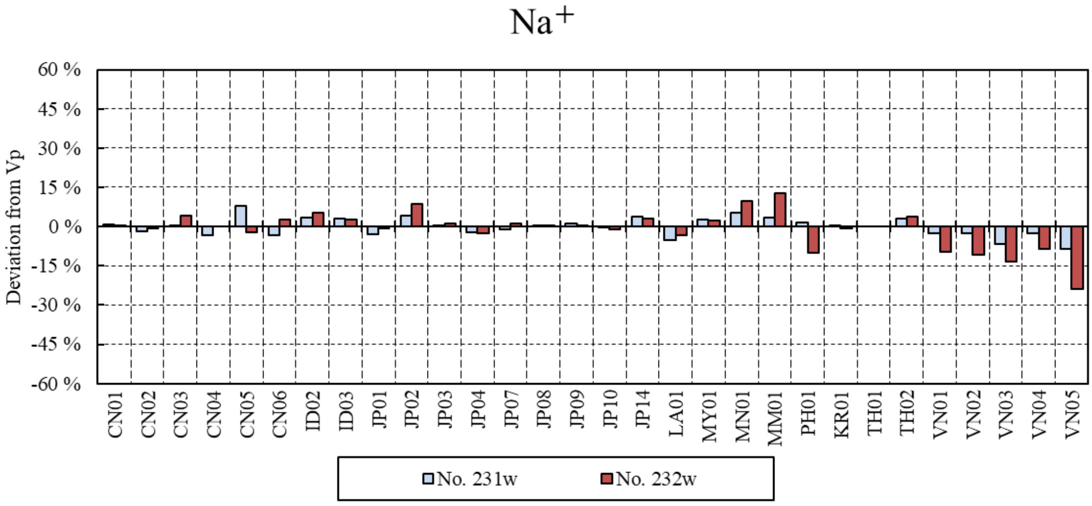


Figure 2.17 Deviation from prepared value for Na^+ (normalized by prepared value)

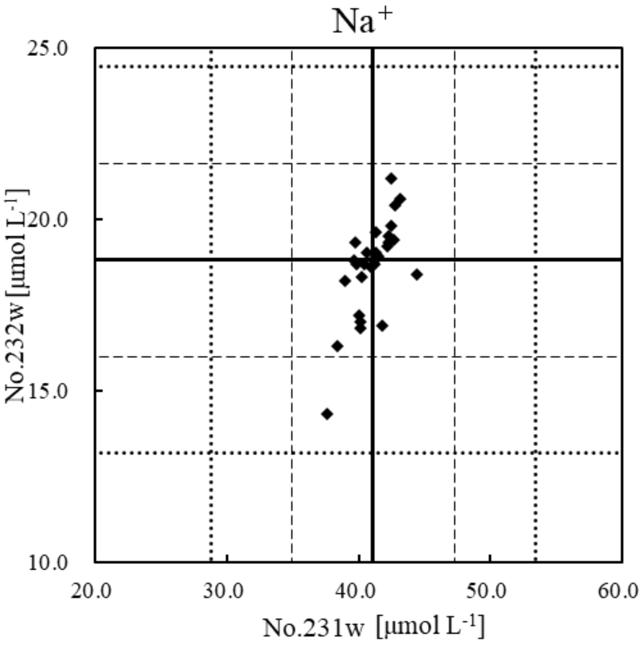


Figure 2.18 Scatter diagram for Na^+

8) K^+

The data of sample No. 231w from 3 laboratories (ID02, JP14 and MN01) and sample No.232w from KR01 were marked with flag “E”. Additionally, the data of sample No. 232w from 5 laboratories (JP14, MN01, PH01, VN03 and VN05) were marked with flag “X”.

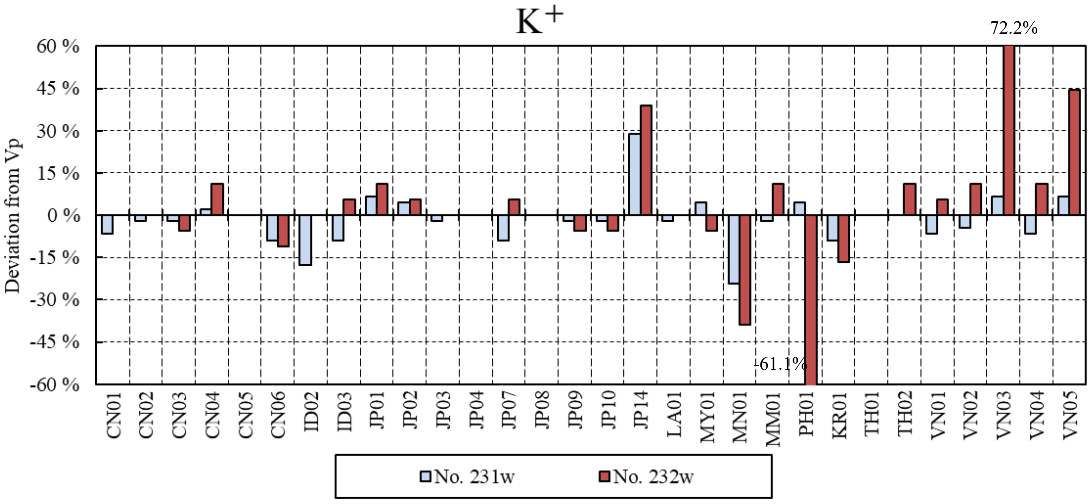


Figure 2.19 Deviation from prepared value for K^+ (normalized by prepared value)

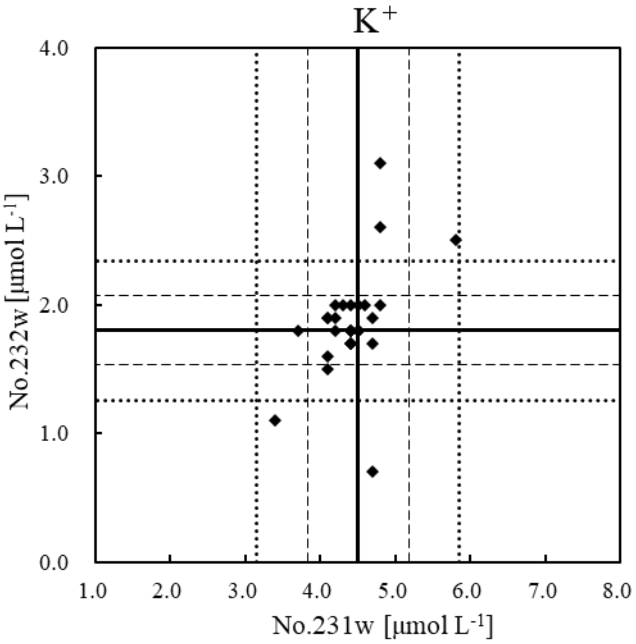


Figure 2.20 Scatter diagram for K^+

9) Ca^{2+}

The data of sample No. 231w from 6 laboratories (PH01, TH02, VN01, VN02, VN03 and VN04) and sample No. 232w from 9 laboratories (CN01, CN02, CN03, CN04, ID02, LA01, MM01, KR01 and VN05) were marked with flag "E". Additionally, the data of sample No.231 from VN05 and No.232w from 3 laboratories (MN01, PH01 and VN03) were marked with flag "X".

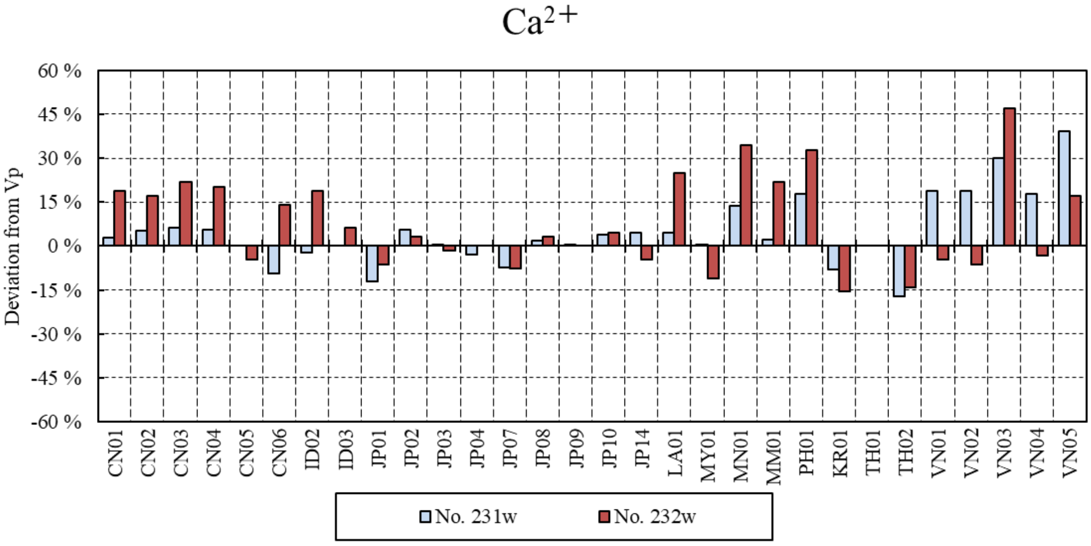


Figure 2.21 Deviation from prepared value for Ca^{2+} (normalized by prepared value)

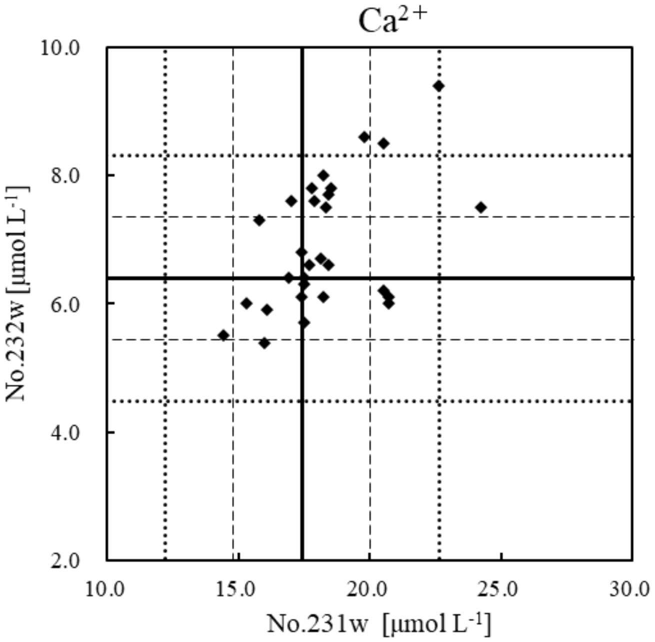


Figure 2.22 Scatter diagram for Ca^{2+}

10) Mg^{2+}

The data of sample No. 231w from 4 laboratories (JP02, PH01, TH02 and VN03) and sample No. 232w from 2 laboratories (JP02 and TH02) were marked with flag “E”.

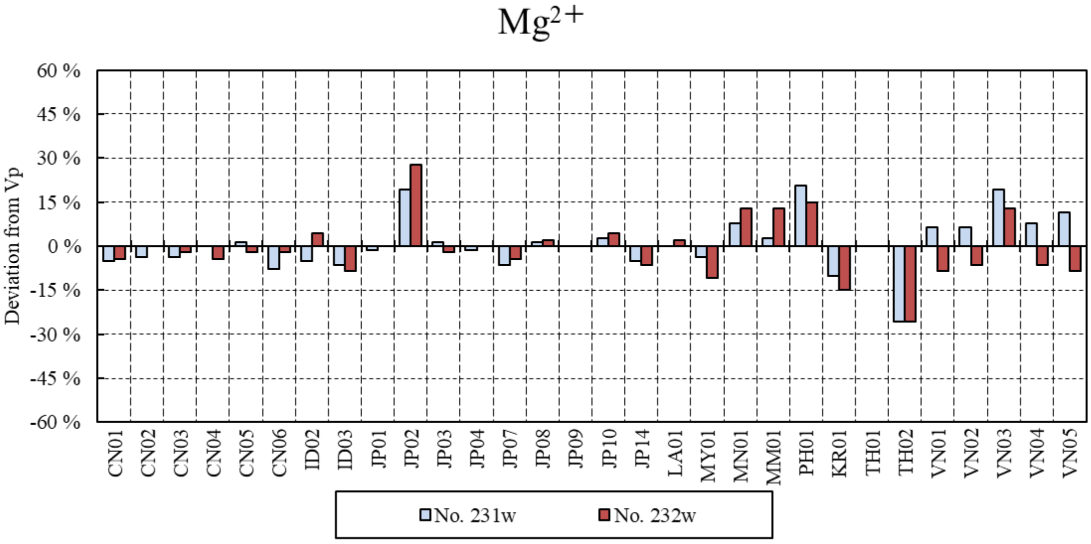


Figure 2.23 Deviation from prepared value for Mg^{2+} (normalized by prepared value)

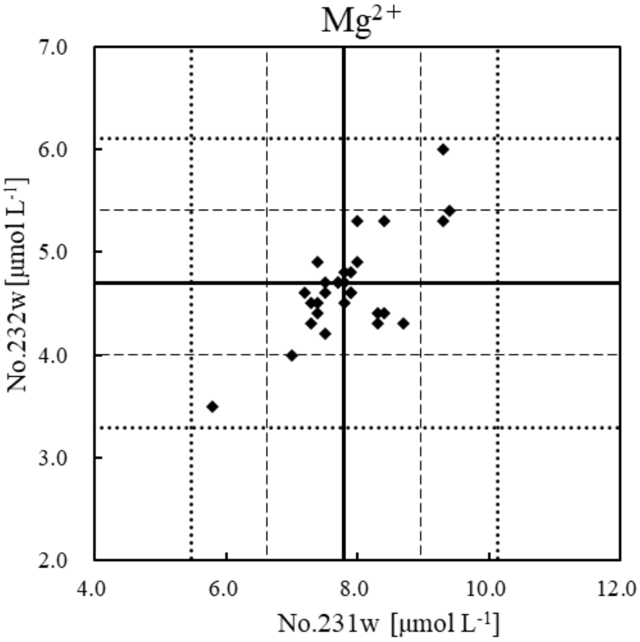


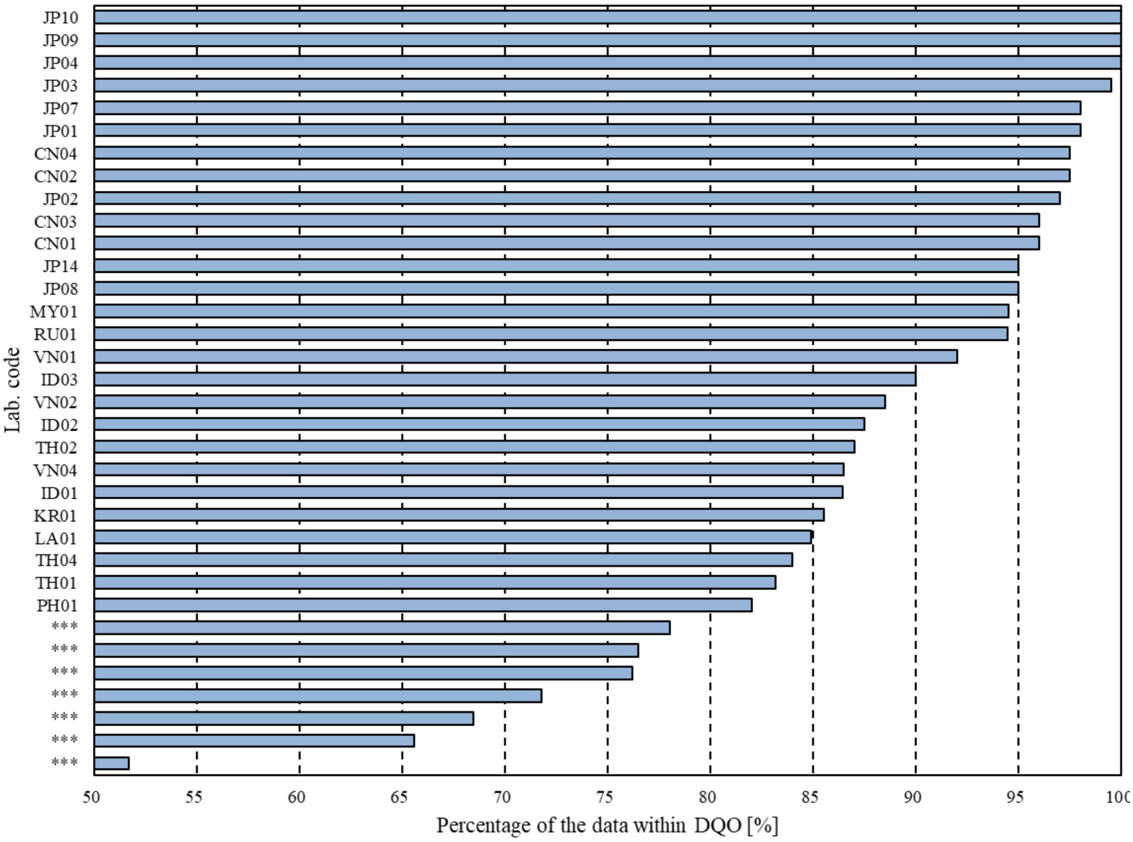
Figure 2.24 Scatter diagram for Mg^{2+}

11) Scatter diagrams

Most of constituents showed positive correlation between the submitted pairs of results of sample No. 231w and 232w. It suggested that systematic error could be the reason for the deviation of results in many of laboratories.

12) Percentage of the data within DQO

Figure 2.25 shows the percentage of the data within DQO for each participating laboratory from 2014 to 2023. All the analytical data of 2 laboratories (JP04, JP09 and JP10) met DQO, while the percentage of the data within DQO in 7 laboratories was below 80%.



Note: Lab. code is indicated as "***" in case that percentage of the data within DQO is below 80%.

Figure 2.25 Percentage of the data within DQO for each participating laboratory (2014-2023)

2.3.3 Sample and analysis evaluation

The concentrations of the analytical parameters in the samples for this survey were determined based on actual EANET monitoring data of wet deposition. Two samples were not distinguished as high or low concentration samples when they were distributed to participating laboratories. Each ion (including pH as H^+) concentrations of sample No. 231w were higher than those of No. 232w.

The relative standard deviations (R.S.D.) of each parameter for sample No. 231w and No. 232w are shown in the Figure 2.26. The R.S.D. values of sample No. 232w were higher than sample No.231w except for pH and NO_3^-. K^+ had the largest R.S.D. value difference between sample No.231w and No. 232w. The R.S.D. of K^+ for sample No. 232w was the largest in this survey.

(Relative standard deviation (%) = (Standard deviation / Average) x100; Reported data after removing the outliers)

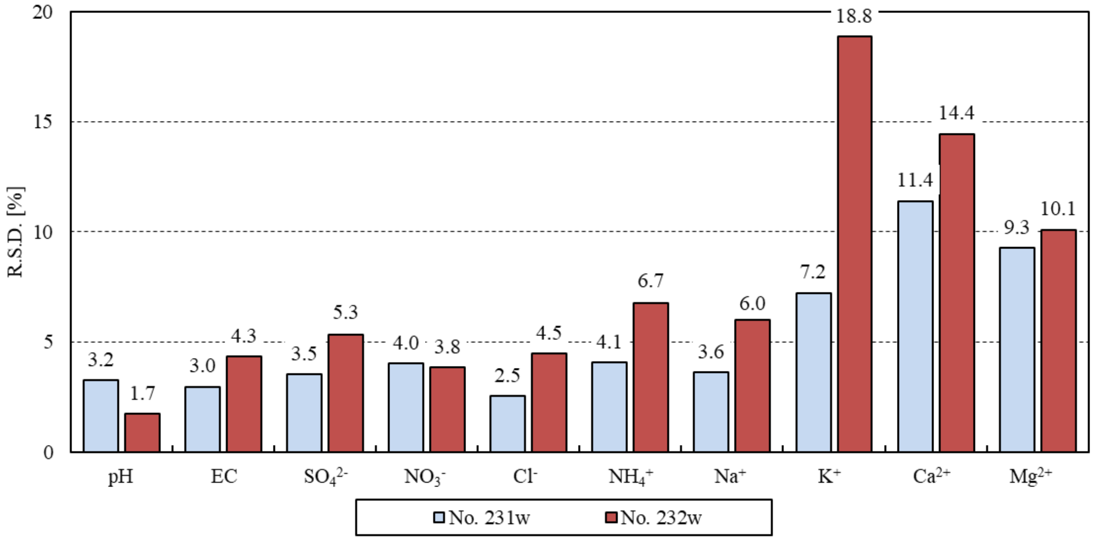


Figure 2.26 Relative standard deviations (R.S.D.) of each parameter

2.3.4 Information on laboratories

1) Number of analysts and their experience

Number of analysts and years of their experience are shown in Table 2.11 and Table 2.12, respectively. In Table 2.11, the letters of “A”, “B”, “C” and “D” refer to individual analysts in each laboratory who carried out analyses. In 14 laboratories, single analyst carried out the analyses for all parameters. No clear relationship between the number of analysts and flagged data was suggested.

Table 2.11 Number of analysts

Lab. ID	Total	pH	EC	SO_4^{2-}	NO_3^-	Cl^-	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}
CN01	2	A	A	B	B	B	B	B	B	B	B
CN02	2	A	A	B	B	B	B	B	B	B	B
CN03	2	A	A	B	B	B	B	B	B	B	B
CN04	1	A	A	A	A	A	A	A	A	A	A
CN05	2	A	A	B	B	B	B	B	B	B	B
CN06	2	A	B	A	A	A	A	A	A	A	A
ID02	4	A	B	C	C	C	D	D	D	D	D
ID03	1	A	A	A	A	A	A	A	A	A	A
JP01	1	A	A	A	A	A	A	A	A	A	A
JP02	1	A	A	A	A	A	A	A	A	A	A
JP03	1	A	A	A	A	A	A	A	A	A	A
JP04	1	A	A	A	A	A	A	A	A	A	A
JP07	1	A	A	A	A	A	A	A	A	A	A
JP08	1	A	A	A	A	A	A	A	A	A	A
JP09	1	A	A	A	A	A	A	A	A	A	A
JP10	1	A	A	A	A	A	A	A	A	A	A
JP14	1	A	A	A	A	A	A	A	A	A	A
LA01	3	---	---	A	A	A	A	B	A	A	C
MY01	3	A	A	B	B	B	C	C	C	C	C
MN01	2	A	A	B	B	B	B	B	B	B	B
MM01	1	A	A	A	A	A	A	A	A	A	A
PH01	4	A	A	B	B	B	C	C	C	C	D
KR01	1	A	A	A	A	A	A	A	A	A	A
TH01	3	A	B	C	C	C	---	---	---	---	---
TH02	1	A	A	A	A	A	A	A	A	A	A
VN01	2	A	A	B	B	B	B	B	B	B	B
VN02	2	A	A	B	B	B	B	B	B	B	B
VN03	2	A	A	B	A	---	A	B	B	B	B
VN04	2	A	A	B	B	B	B	B	B	B	B
VN05	2	A	A	B	B	B	B	B	B	B	B

Note: Light mesh, Analytic data of sample No. 231w or No. 232w was marked with flag "E" or "X";
Dark mesh, Analytic data of both samples were marked with flag "E" or "X";
"---", Not measured

212 data out of all the submitted data (584), were analyzed by the analysts whose experience was less than 5 years, and they account for 36.3%. No clear relationship between the years of experience and flagged data was suggested.

Table 2.12 Years of experience

Lab. ID	pH	EC	SO_4^{2-}	NO_3^{-}	Cl^{-}	NH_4^{+}	Na^{+}	K^{+}	Ca^{2+}	Mg^{2+}
CN01	2	2	1	1	1	1	1	1	1	1
CN02	5	5	5	5	5	5	5	5	5	5
CN03	11	11	25	25	25	25	25	25	25	25
CN04	15	15	15	15	15	15	15	15	15	15
CN05	5	5	7	7	7	7	7	7	7	7
CN06	6	2	6	6	6	6	6	6	6	6
ID02	1	3	16	16	16	16	16	16	16	16
ID03	19	19	19	19	19	19	19	19	19	19
JP01	20	20	20	20	20	20	20	20	20	20
JP02	1	1	1	1	1	1	1	1	1	1
JP03	2	2	2	2	2	2	2	2	2	2
JP04	6	6	6	6	6	6	6	6	6	6
JP07	1	1	1	1	1	1	1	1	1	1
JP08	2	2	2	2	2	2	2	2	2	2
JP09	9	9	9	9	9	9	9	9	9	9
JP10	4	4	4	4	4	4	4	4	4	4
JP14	1	1	1	1	1	1	1	1	1	1
LA01	---	---	4	4	4	4	4	4	4	4
MY01	10	10	11	11	11	1	1	1	1	1
MN01	16	16	20	20	20	20	20	20	20	20
MM01	2	2	2	2	2	2	2	2	2	2
PH01	2	2	1	1	1	4	5	5	5	4
KR01	18	18	18	18	18	18	18	18	18	18
TH01	25	25	1	1	1	---	---	---	---	---
TH02	25	25	25	25	25	25	25	25	25	25
VN01	7	7	10	10	10	10	10	10	10	10
VN02	14	14	10	10	10	10	10	10	10	9
VN03	9	9	12	9	---	9	12	12	12	12
VN04	19	19	19	19	19	19	19	19	19	19
VN05	11	11	16	16	16	16	16	16	16	16

Note: Light mesh, Analytic data of sample No. 231w or No. 232w was marked with flag "E" or "X";
Dark mesh, Analytic data of both samples were marked with flag "E" or "X";
"---", Not measured

2) Analytical instruments

As shown in Figure 2.27, all the participating laboratories used the recommended methods described in *Technical Manual for Wet Deposition Monitoring in East Asia -2010*. The method list is shown in Table 2.3. Analytical methods used for the measurement in the participating laboratories are shown in Table 2.13. No clear relationship between analytical methods and flagged data was suggested.

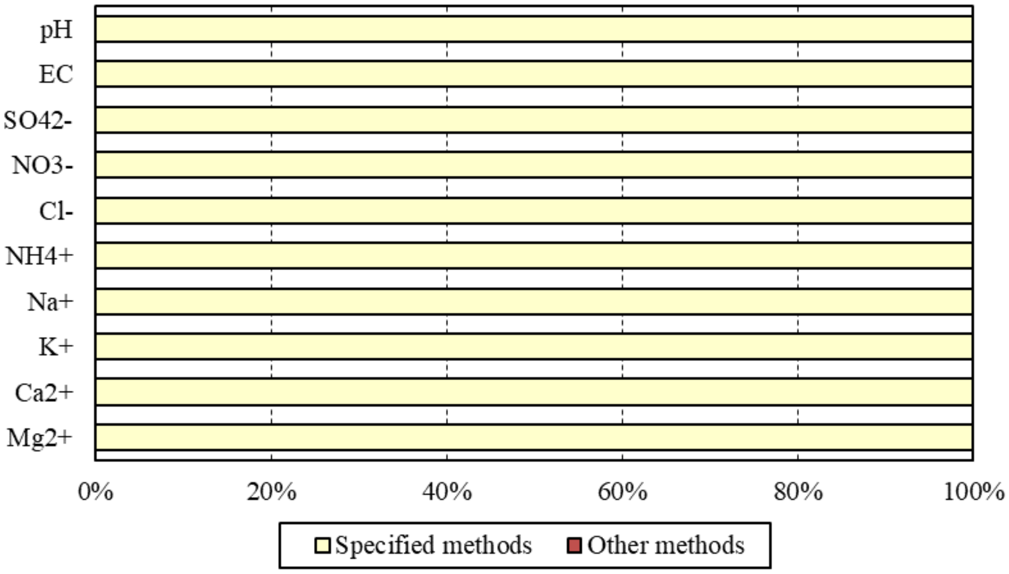


Figure 2.27 Percentage of laboratories that use the recommended methods

Table 2.13 Analytical method used for the measurement in the participating laboratories

Lab. ID	SO_4^{2-}	NO_3^-	Cl^-	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}
CN01	IC	IC	IC	IC	IC	IC	IC	IC
CN02	IC	IC	IC	IC	IC	IC	IC	IC
CN03	IC	IC	IC	IC	IC	IC	IC	IC
CN04	IC	IC	IC	IC	IC	IC	IC	IC
CN05	IC	IC	IC	IC	IC	IC	IC	IC
CN06	IC	IC	IC	IC	IC	IC	IC	IC
ID02	IC	IC	IC	IC	IC	IC	IC	IC
ID03	IC	IC	IC	IC	IC	IC	IC	IC
JP01	IC	IC	IC	IC	IC	IC	IC	IC
JP02	IC	IC	IC	IC	IC	IC	IC	IC
JP03	IC	IC	IC	IC	IC	IC	IC	IC
JP04	IC	IC	IC	IC	IC	IC	IC	IC
JP07	IC	IC	IC	IC	IC	IC	IC	IC
JP08	IC	IC	IC	IC	IC	IC	IC	IC
JP09	IC	IC	IC	IC	IC	IC	IC	IC
JP10	IC	IC	IC	IC	IC	IC	IC	IC
JP14	IC	IC	IC	IC	IC	IC	IC	IC
LA01	IC	IC	IC	IC	IC	IC	IC	IC
MY01	IC	IC	IC	IC	IC	IC	IC	IC
MN01	IC	IC	IC	IC	IC	IC	IC	IC
MM01	IC	IC	IC	IC	IC	IC	IC	IC
PH01	IC	IC	IC	SP	AAS	AAS	AAS	AAS
KR01	IC	IC	IC	IC	IC	IC	IC	IC
TH01	IC	IC	IC	---	---	---	---	---
TH02	IC	IC	IC	IC	IC	IC	IC	IC
VN01	IC	IC	IC	IC	IC	IC	IC	IC
VN02	IC	IC	IC	IC	IC	IC	IC	IC
VN03	SP	SP	---	SP	AES	AES	AES	AES
VN04	IC	IC	IC	IC	IC	IC	IC	IC
VN05	IC	IC	IC	IC	IC	IC	IC	IC

Note: "---" Not measured

IC: Ion Chromatography	AAS: Atomic Absorption Spectrometry
AES: Atomic Emission Spectrometry	SP: Spectrophotometry(Indophenol)
SP*: Spectrophotometry(Others)	TI: Titrimetry

3) Date of analysis

Figure 2.28 shows the distribution of “Start date” and “Finish date” of analysis at the participating laboratories. In total, 67% of all the submitted data was determined by the end of 2023, and 10% was determined later than the submission deadline of this project.

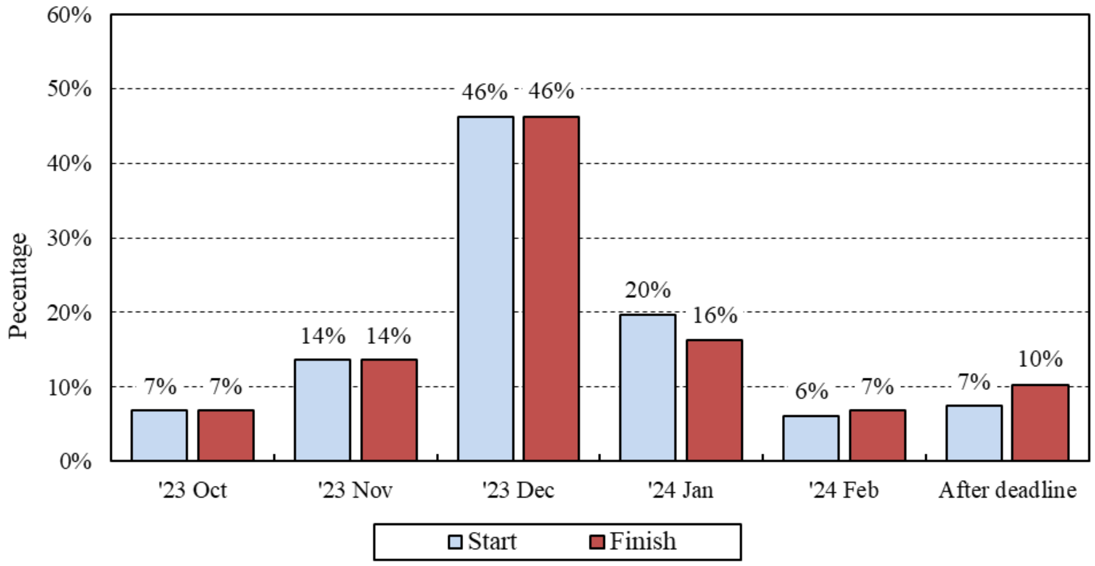


Figure 2.28 Distribution of start date and finish date of analysis

Figure 2.29 shows the number of days required to determine the analytical data at the participating laboratories. Most analytical data were obtained within less than 3 days.

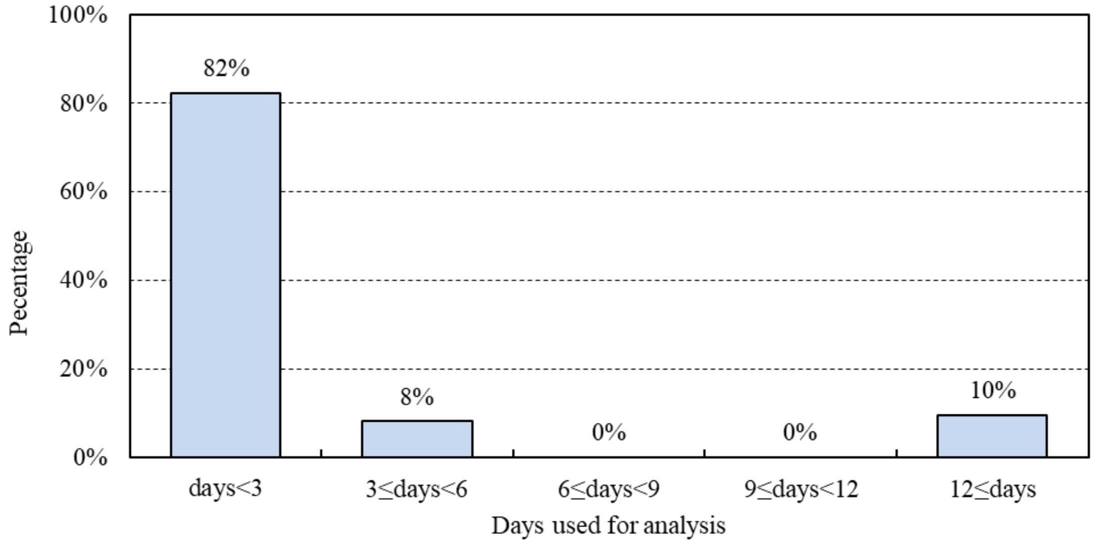


Figure 2.29 Distribution of days used for analysis

No clear relationship between date of analysis and flagged data was suggested, however, it is recommended analyzing the samples as soon as possible once they arrive at each laboratory.

2.4 Comparison with past surveys

Since the beginning of EANET, the inter-laboratory comparison on wet deposition has reached the 26th survey. The percentages of data within DQO and prepared value of EC are shown in Figure 2.30. Hereafter, sample No. 231w and No. 232w are treated as high and low concentration samples, respectively.

The percentage of data within DQO for the sample No. 231w and No. 232w were 94.5% and 90.4%, respectively. As shown in this figure, low concentration samples show a tendency that the percentages of data within DQO are dependent on the prepared values of EC.

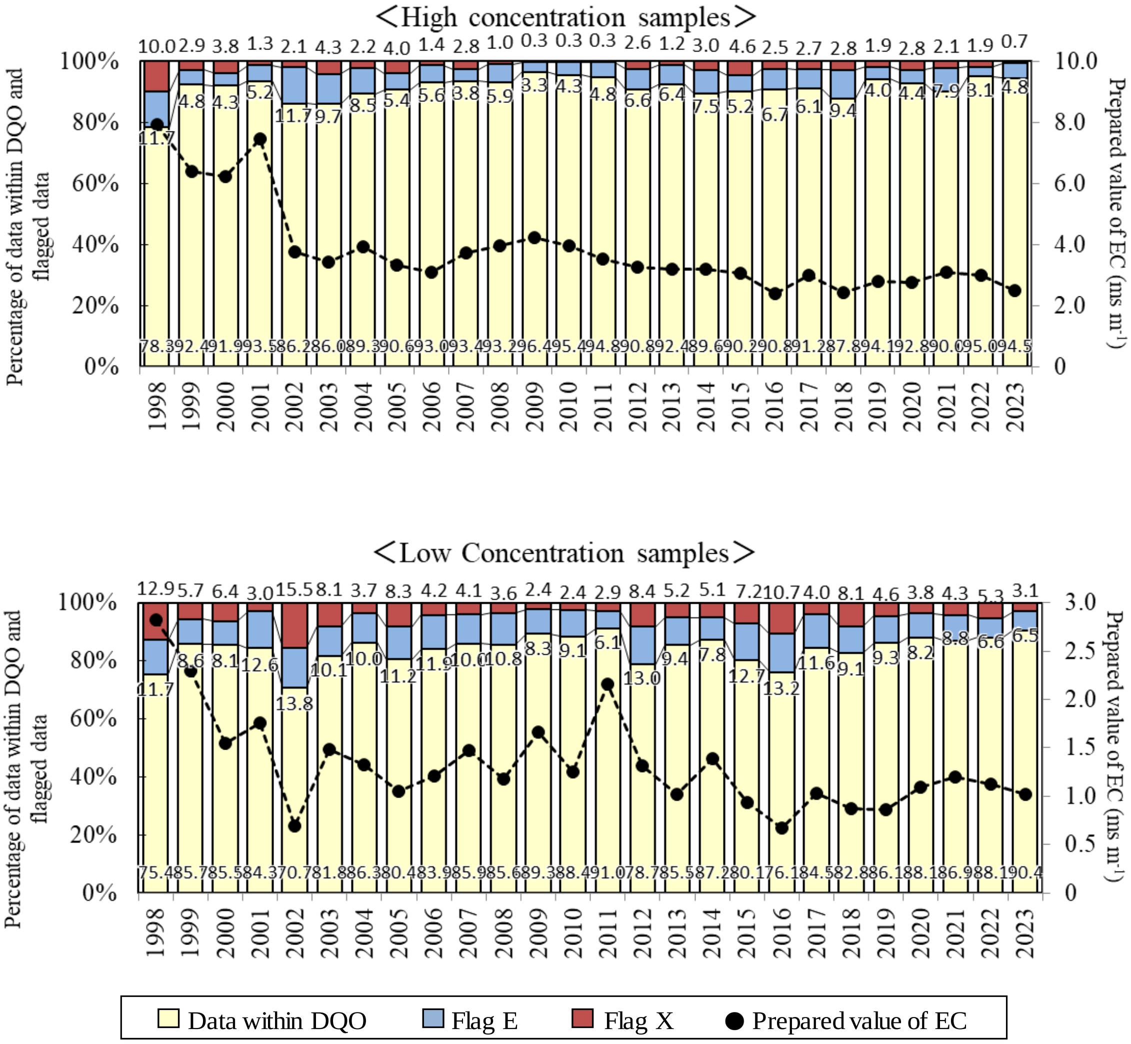


Figure 2.30 Comparison of results from the inter-laboratory comparison projects

Figure 2.31 shows the trend of the prepared values and the percentage of the flagged data. There is a tendency that cations have more flagged data than anions throughout the series of survey.

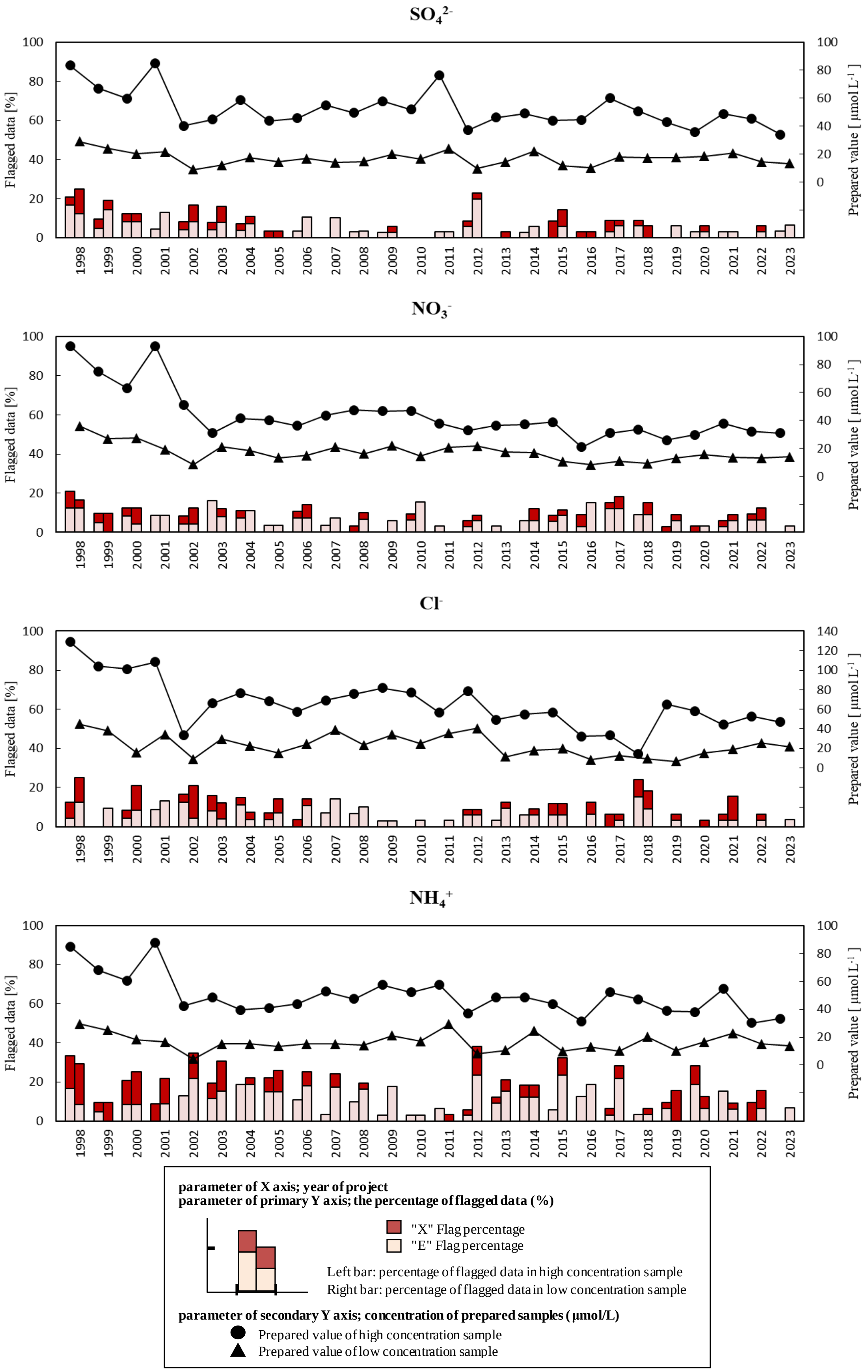


Figure 2.31 Comparison for each parameter in inter-laboratory comparison (ILC) project

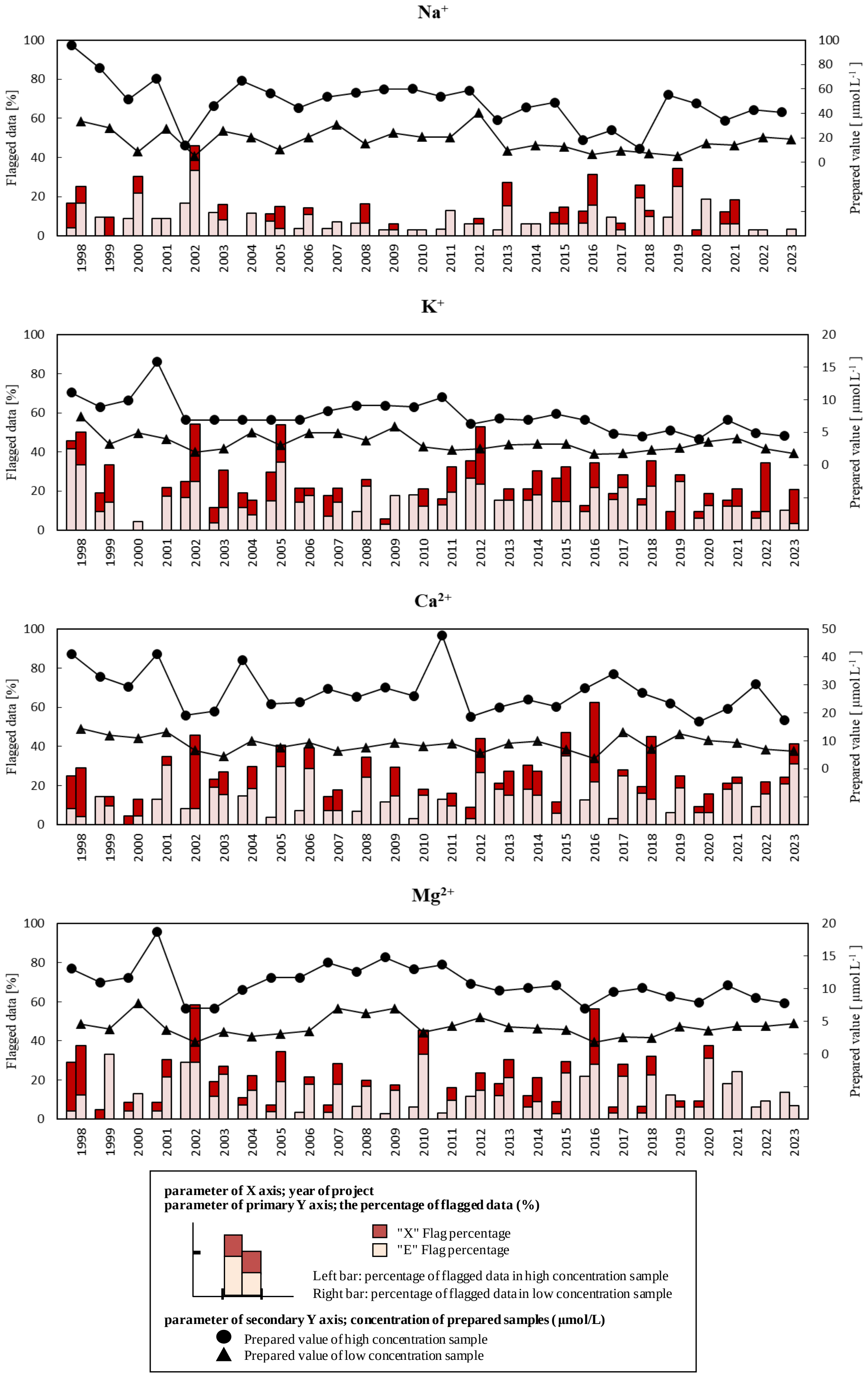


Figure 2.31 Comparison for each parameter in ILC project (continued)

As shown in figure 2.32, the total number of data in this survey was 584.

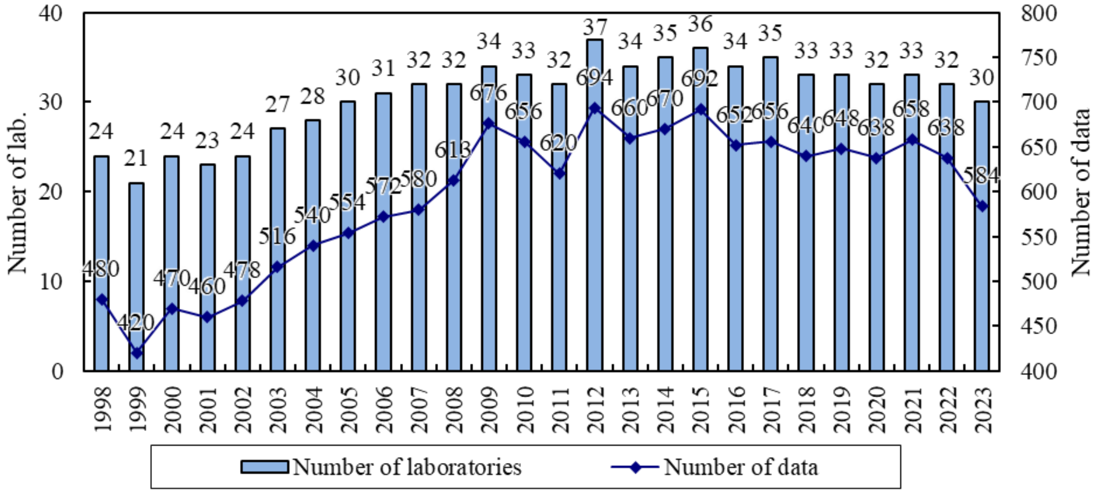


Figure 2.32 The number of participating laboratories and data in the inter-laboratory comparison projects on wet deposition

2.5 Recommendations for improvement

The fundamental matters for QA/QC on measurements and analyses of samples are described in *Technical Manual for Wet Deposition Monitoring in East Asia -2010*.
Additionally, the NC showed the following matters for the improvement of data accuracy.

2.5.1 Measurement and Analysis

► *Technical Manual for Wet Deposition Monitoring in East Asia -2010* defined EANET DQO values for Detection limits and Determination limits. But both limits exceed the DQO in some laboratories. Both limits depend on the standard deviation from five times analysis of the standard solution which has concentration levels near determination limit of the analytical method. The standard deviation can be improved by method such as use of more purified water. Then Detection limits and Determination limits would be improved.

► Before analysis, it is important to make sure that every experimental instrument is kept clean. Otherwise, contamination would be likely to occur, which leads to increase the blank values. High blank values could adversely affect the quality of analytical data, so careful and diligent cleaning is strongly recommended from the point of view of QA/QC.

2.5.2 Data control

► After determining all the analytical parameters, the data check by calculating R_1 and R_2 values is important. Especially, R_1 and R_2 must meet allowable ranges according to *Technical Manual for Wet Deposition Monitoring in East Asia -2010*. If the values exceed their allowable ranges, the data set is doubtful, and reanalysis shall be carried out after rechecking analytical instruments and analytical procedures.

► Participating laboratories are encouraged to check precision of results in prior to submission. It should be noted that precision is greatly affected by concentration. To grasp the state of precision, drawing correlation curve between concentration and precision is effective.

► After ILC was done, artificial samples can be used as Standard Reference Material as described in *Technical Manual for Wet Deposition Monitoring in East Asia -2010*. The concentration of artificial samples will be stable until next ILC when they are preserved in the refrigerator. Each laboratory should measure Standard Reference Materials in the analytical sample stream.

References

EANET (2010). *Technical Manual for Wet Deposition Monitoring in East Asia -2010*. Asia Center for Air Pollution Research, Niigata, Japan, 113p.

Appendix 2.1 Data precision of submitted data

Data precision is one of the most important factors of data quality. Relative standard deviation (R.S.D.), which is one of the parameters to indicate precision, is defined by the equation below.

R.S.D. = σ / Va × 100%
σ: standard deviation of result Va: average of result

In Appendix Table 2.1.1 and Appendix Table 2.1.2, data precisions calculated from the submitted results are shown. There is a tendency that each constituent of higher concentration sample (No. 231w) shows better R.S.D. than that of lower concentration sample (No. 232w) . This suggests that R.S.D. are greatly affected by sample concentrations.

Participating laboratories are encouraged to check the precision of data in prior to submission. Correlation between sample concentration and precision should be also noted, because sample concentration could be the greatest factor to determine precision. Therefore, it is important to grasp the state of data quality during daily analysis. For example, drawing a correlation curve between concentration of standard solutions and R.S.D. of repeat analysis is effective.

Appendix Table 2.1.1 Data precision (R.S.D.) of sample No. 231w

Lab. ID	pH as H^+	EC	SO_4^{2-}	NO_3^-	Cl^-	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}
	%	%	%	%	%	%	%	%	%	%
CN01	1.2	0.6	0.2	0.2	0.2	0.4	0.4	1.1	0.5	0.4
CN02	0.9	0.2	0.1	0.2	0.1	0.2	0.1	0.0	0.3	0.0
CN03	1.3	0.3	0.2	0.2	0.2	0.3	0.2	1.8	0.4	1.2
CN04	1.4	0.3	0.3	0.2	0.4	0.0	1.9	0.0	0.9	0.0
CN05	0.0	0.0	0.1	0.3	0.0	0.0	0.0	2.2	0.6	0.0
CN06	1.2	0.2	0.6	1.0	1.0	0.7	0.1	1.6	1.2	1.2
ID02	1.3	0.2	0.1	0.2	0.2	0.0	0.0	0.0	0.0	0.0
ID03	8.8	0.6	2.9	3.3	2.3	2.0	2.0	11.4	3.8	4.9
JP01	3.3	0.8	0.7	1.0	0.8	2.3	0.7	1.4	0.7	0.8
JP02	1.0	0.3	0.2	0.2	0.2	0.8	0.8	2.1	1.2	1.4
JP03	2.7	0.5	0.3	0.2	0.2	0.3	0.2	0.0	0.3	0.4
JP04	1.8	0.2	0.3	0.3	0.3	0.4	0.2	1.5	0.3	0.9
JP07	2.4	0.5	0.1	0.2	0.2	0.2	0.2	1.2	0.4	0.7
JP08	4.8	1.1	0.2	0.2	0.2	0.2	0.1	1.5	1.1	1.5
JP09	1.6	0.3	0.1	0.2	0.1	0.2	0.1	1.0	0.0	0.0
JP10	0.6	0.5	0.3	0.2	0.2	0.6	0.6	0.8	0.6	0.6
JP14	26.7	1.6	0.5	1.4	0.6	1.7	3.0	14.4	0.6	0.4
LA01	--	--	1.8	1.4	1.1	1.9	3.0	4.2	5.1	2.4
MY01	2.1	0.4	0.3	0.4	0.5	0.6	1.0	5.7	1.9	2.2
MN01	10.0	1.5	1.3	4.6	1.3	2.6	1.6	5.6	1.7	1.9
MM01	21.9	8.2	1.1	1.3	1.0	11.9	10.7	11.8	11.7	6.5
PH01	5.3	0.9	0.3	2.2	1.2	1.4	0.7	0.9	4.9	12.7
KR01	7.4	1.2	1.2	1.5	1.5	0.6	1.3	6.3	1.6	1.2
TH01	1.2	0.0	0.2	0.4	0.7	--	--	--	--	--
TH02	6.6	0.7	0.2	0.1	0.2	1.8	0.7	3.6	2.5	1.5
VN01	3.0	0.5	0.5	0.8	0.3	0.4	0.4	3.2	1.3	1.7
VN02	3.1	0.5	0.5	0.4	0.2	0.4	0.2	2.5	0.6	1.5
VN03	2.1	0.2	0.3	0.8	--	0.5	0.4	3.2	0.6	0.7
VN04	9.5	0.8	0.5	1.4	0.4	0.4	0.3	2.2	1.3	0.9
VN05	2.4	0.0	1.7	1.1	1.0	0.9	0.8	1.9	3.4	6.7
Number of data	29	29	30	30	29	29	29	29	29	29
Minimum	0.0	0.0	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0
25% value	1.3	0.2	0.2	0.2	0.2	0.3	0.2	1.1	0.5	0.4
Median	2.4	0.5	0.3	0.4	0.3	0.5	0.4	1.9	0.9	1.2
75% value	5.3	0.8	0.6	1.2	1.0	1.4	1.0	3.6	1.7	1.7
Maximum	26.7	8.2	2.9	4.6	2.3	11.9	10.7	14.4	11.7	12.7

Note: R.S.D was calculated from three reported measurement.

R.S.D for "pH as H^+" was calculated after pH value was converted to H^+ concentration;

"--", Not measured

Appendix Table 2.1.2 Data precision (R.S.D.) of sample No. 232w

Lab. ID	pH as H^+	EC	SO_4^{2-}	NO_3^-	Cl^-	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}
	%	%	%	%	%	%	%	%	%	%
CN01	0.8	0.5	0.7	0.5	0.1	1.4	0.6	4.6	2.3	1.5
CN02	0.9	0.5	0.5	0.3	0.3	0.4	0.3	0.0	0.0	0.0
CN03	1.7	0.7	0.6	0.6	0.4	0.6	0.4	3.9	0.7	1.9
CN04	1.4	0.6	0.0	0.6	0.7	1.9	1.7	0.0	0.0	0.0
CN05	0.0	0.0	0.3	0.5	0.5	0.0	1.1	0.0	2.5	0.0
CN06	0.9	0.8	1.2	2.5	1.7	0.6	3.4	3.4	4.0	4.3
ID02	0.8	0.5	0.3	0.5	0.2	0.0	0.0	0.0	0.0	0.0
ID03	4.2	5.0	2.6	5.3	5.9	7.7	2.3	13.9	4.4	8.3
JP01	2.6	1.0	0.9	0.7	0.9	1.0	0.9	3.9	0.9	0.7
JP02	2.0	0.8	0.4	0.0	0.2	1.5	1.5	3.6	3.4	5.4
JP03	3.0	0.9	0.4	0.6	0.3	0.4	0.2	2.8	0.0	0.0
JP04	1.9	0.6	0.5	0.4	0.4	0.4	0.2	2.7	1.9	1.1
JP07	4.3	0.4	0.4	0.4	0.2	0.4	0.5	0.0	0.9	0.0
JP08	5.6	0.9	0.4	0.4	0.3	0.7	0.7	0.0	1.3	1.9
JP09	4.8	0.4	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0
JP10	1.3	0.0	0.0	0.6	0.3	1.0	0.3	3.0	0.7	0.0
JP14	16.9	1.5	0.5	0.7	0.5	1.4	2.6	11.5	2.4	1.6
LA01	--	--	1.9	2.5	1.3	1.9	2.4	9.9	4.2	2.3
MY01	2.9	0.4	0.4	0.3	0.5	0.9	2.0	3.0	4.6	4.8
MN01	13.0	2.5	1.4	1.5	1.4	5.2	5.0	9.0	5.8	2.3
MM01	30.6	22.5	1.6	1.6	1.3	3.0	2.2	7.0	3.9	3.8
PH01	11.2	2.2	0.6	0.9	1.0	1.2	1.2	7.1	12.1	15.4
KR01	8.2	4.6	1.1	0.9	1.2	1.5	1.2	5.3	1.3	1.1
TH01	0.0	0.5	0.5	0.3	0.5	--	--	--	--	--
TH02	8.0	1.5	0.4	0.4	0.2	1.5	0.6	4.9	9.5	2.8
VN01	3.8	1.3	1.1	1.4	0.6	1.2	0.9	8.1	3.5	3.2
VN02	4.2	1.2	1.0	0.9	0.6	0.9	0.7	6.1	2.0	3.3
VN03	1.3	6.2	0.5	0.4	--	0.4	0.6	1.1	1.2	2.7
VN04	4.5	1.0	0.8	0.8	0.3	0.7	0.7	3.6	1.3	1.1
VN05	4.0	0.0	6.8	3.3	2.0	2.2	3.3	1.9	3.4	1.9
Number of data	29	29	30	30	29	29	29	29	29	29
Minimum	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
25% value	1.3	0.5	0.4	0.4	0.3	0.4	0.5	1.1	0.9	0.0
Median	3.0	0.8	0.5	0.6	0.5	1.0	0.9	3.6	2.0	1.9
75% value	4.8	1.5	1.1	0.9	1.0	1.5	2.0	6.1	3.9	3.2
Maximum	30.6	22.5	6.8	5.3	5.9	7.7	5.0	13.9	12.1	15.4

Note: R.S.D was calculated from three reported measurement.

R.S.D for "pH as H^+" was calculated after pH value was converted to H^+ concentration;

"--", Not measured

Appendix 2.2 Deviation% from prepared values

Appendix Table 2.2.1 Deviation% from prepared values of sample No. 231w

Lab. ID	pH	EC	SO_4^{2-}	NO_3^-	Cl^-	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}
	%	%	%	%	%	%	%	%	%	%
CN01	0.0	-4.0	-0.6	4.5	-0.2	-1.5	0.7	-6.7	2.9	-5.1
CN02	0.8	-1.6	-0.6	-1.0	-0.2	0.0	-1.7	-2.2	5.2	-3.8
CN03	0.4	-1.6	-2.6	-1.3	0.4	0.0	0.5	-2.2	6.3	-3.8
CN04	1.0	0.0	1.5	-1.6	0.6	-3.3	-3.4	2.2	5.7	0.0
CN05	1.0	-3.6	2.1	0.6	0.6	0.0	8.0	0.0	0.0	1.3
CN06	2.5	-3.6	-3.8	-1.3	0.8	0.0	-3.2	-8.9	-9.2	-7.7
ID02	1.0	-5.6	12.3	8.0	12.1	-9.9	3.4	-17.8	-2.3	-5.1
ID03	0.8	-9.2	15.8	9.0	5.1	-4.2	2.9	-8.9	0.0	-6.4
JP01	1.9	-1.2	-0.3	1.9	-1.3	-4.2	-2.9	6.7	-12.1	-1.3
JP02	0.8	-3.2	-0.6	0.6	1.7	3.9	4.1	4.4	5.7	19.2
JP03	0.2	0.4	1.2	1.0	0.6	0.3	0.5	-2.2	0.6	1.3
JP04	-0.8	0.0	0.6	-0.3	-1.7	0.9	-2.2	0.0	-2.9	-1.3
JP07	0.6	2.4	0.3	-1.3	0.0	3.6	-1.2	-8.9	-7.5	-6.4
JP08	0.6	-4.0	-0.9	-0.3	0.8	0.6	0.5	0.0	1.7	1.3
JP09	1.7	-1.2	0.0	0.0	-0.2	-0.9	1.0	-2.2	0.6	0.0
JP10	0.6	0.4	1.8	0.0	-1.3	-3.6	-0.5	-2.2	4.0	2.6
JP14	6.5	-4.8	5.6	5.5	4.7	-2.7	3.9	28.9	4.6	-5.1
LA01	---	---	-7.3	-7.7	-8.1	-1.5	-5.1	-2.2	4.6	0.0
MY01	1.7	-2.0	-1.5	-2.6	-0.8	6.6	2.7	4.4	0.6	-3.8
MN01	-7.3	-5.6	-0.3	7.4	2.3	3.0	5.1	-24.4	13.8	7.7
MM01	3.6	-52.2	-2.1	-4.2	0.6	7.2	3.4	-2.2	2.3	2.6
PH01	0.6	-6.0	3.8	-2.9	-0.8	1.2	1.7	4.4	17.8	20.5
KR01	1.7	-5.6	-3.8	-3.2	-1.7	-3.3	0.2	-8.9	-8.0	-10.3
TH01	-0.2	-1.2	-4.4	10.9	-2.3	---	---	---	---	---
TH02	1.9	-4.8	1.8	1.0	1.1	-6.0	2.9	0.0	-17.2	-25.6
VN01	9.4	-6.8	-1.8	0.0	-2.3	-6.3	-2.4	-6.7	19.0	6.4
VN02	9.2	-7.2	-2.9	1.3	-0.8	-6.9	-2.4	-4.4	19.0	6.4
VN03	0.8	-5.6	-2.3	-0.6	---	-2.7	-6.6	6.7	29.9	19.2
VN04	9.6	-6.4	-0.9	-1.6	-4.7	-5.7	-2.7	-6.7	17.8	7.7
VN05	0.2	-7.6	-3.2	-2.9	3.2	4.5	-8.5	6.7	39.1	11.5
Number of data	29	29	30	30	29	29	29	29	29	29
Average	1.8	-5.2	0.2	0.6	0.3	-1.1	0.0	-1.8	4.9	0.8
Minimum	-7.3	-52.2	-7.3	-7.7	-8.1	-9.9	-8.5	-24.4	-17.2	-25.6
Maximum	9.6	2.4	15.8	10.9	12.1	7.2	8.0	28.9	39.1	20.5

Note: "---", Not measured

Appendix Table 2.2.2 Deviation% from prepared values of sample No. 232w

Lab. ID	pH	EC	SO_4^{2-}	NO_3^-	Cl^-	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}
	%	%	%	%	%	%	%	%	%	%
CN01	-0.4	0.0	4.5	2.8	2.3	2.9	0.5	0.0	18.8	-4.3
CN02	0.2	2.9	9.1	0.0	0.0	2.2	-0.5	0.0	17.2	0.0
CN03	3.1	0.0	6.8	-2.8	1.4	3.7	4.3	-5.6	21.9	-2.1
CN04	1.3	0.0	0.0	-2.8	0.5	0.0	0.0	11.1	20.3	-4.3
CN05	-0.2	-2.0	2.3	0.7	0.9	-2.2	-2.1	0.0	-4.7	-2.1
CN06	1.0	-1.0	-5.3	0.0	0.9	0.7	2.7	-11.1	14.1	-2.1
ID02	-0.6	-2.9	24.2	17.7	13.8	-4.4	5.3	0.0	18.8	4.3
ID03	-0.2	7.8	15.9	6.4	-0.5	-14.7	2.7	5.6	6.3	-8.5
JP01	1.3	5.9	0.0	5.0	1.4	0.7	-0.5	11.1	-6.3	0.0
JP02	-0.6	1.0	1.5	0.0	-0.5	6.6	8.5	5.6	3.1	27.7
JP03	-1.9	8.8	2.3	2.8	1.4	2.2	1.1	0.0	-1.6	-2.1
JP04	-1.1	2.9	1.5	0.7	-1.8	0.7	-2.7	0.0	0.0	0.0
JP07	-0.6	9.8	-0.8	-2.1	0.0	1.5	1.1	5.6	-7.8	-4.3
JP08	-0.4	-3.9	0.8	0.0	0.0	0.7	0.5	0.0	3.1	2.1
JP09	0.4	2.9	0.8	0.7	0.0	0.7	0.5	-5.6	0.0	0.0
JP10	-0.8	5.9	1.5	0.0	-2.3	-2.9	-1.1	-5.6	4.7	4.3
JP14	3.8	0.0	9.1	8.5	8.7	1.5	3.2	38.9	-4.7	-6.4
LA01	---	---	-7.6	-9.9	-10.6	11.8	-3.2	0.0	25.0	2.1
MY01	1.1	2.9	-7.6	-5.7	-2.3	19.9	2.1	-5.6	-10.9	-10.6
MN01	-10.0	2.9	0.0	6.4	3.2	-0.7	9.6	-38.9	34.4	12.8
MM01	3.3	-41.2	-0.8	-2.1	-0.9	19.9	12.8	11.1	21.9	12.8
PH01	0.0	-2.9	-1.5	-2.8	7.3	3.7	-10.1	-61.1	32.8	14.9
KR01	0.4	2.9	-3.0	-2.1	-0.9	6.6	-0.5	-16.7	-15.6	-14.9
TH01	-1.7	2.0	-12.1	6.4	-6.0	---	---	---	---	---
TH02	0.0	0.0	1.5	-0.7	1.4	0.0	3.7	11.1	-14.1	-25.5
VN01	3.4	-5.9	-0.8	-2.1	-4.1	-2.9	-9.6	5.6	-4.7	-8.5
VN02	3.8	-6.9	0.0	-1.4	-4.6	-2.2	-10.6	11.1	-6.3	-6.4
VN03	0.0	-5.9	0.0	1.4	---	-8.1	-13.3	72.2	46.9	12.8
VN04	3.6	-4.9	0.0	-2.8	-4.1	-4.4	-8.5	11.1	-3.1	-6.4
VN05	-2.1	-2.9	-4.5	2.1	-17.9	5.9	-23.9	44.4	17.2	-8.5
Number of data	29	29	30	30	29	29	29	29	29	29
Average	0.2	-0.7	1.3	0.8	-0.5	1.7	-1.0	3.3	7.8	-0.8
Minimum	-10.0	-41.2	-12.1	-9.9	-17.9	-14.7	-23.9	-61.1	-15.6	-25.5
Maximum	3.8	9.8	24.2	17.7	13.8	19.9	12.8	72.2	46.9	27.7

Note: "---", Not measured

3. 19th INTER-LABORATORY COMPARISON PROJECT ON DRY DEPOSITION

3.1 Introduction

In the Inter-laboratory Comparison on dry deposition, impregnated filters which contained either $SO_4^{2-}$and Cl^-, or NH_4^+, were prepared and distributed to the participating laboratories by the Network Center (NC) in October 2023. Most of the laboratories which monitor with the filter pack method in EANET joined this activity and submitted their analytical results to the NC. These results were compared with the corresponding prepared value and statistically analyzed.

3.2 Procedures

3.2.1 Participating Laboratories

A total of 20 laboratories in charge of EANET dry deposition monitoring participated in this 19th activity and 18 laboratories submitted the results to the NC. The participating laboratories and data submission status are shown in Table 1.1.

3.2.2 Description of Samples

Two kinds of filter samples, one contained two ions (SO_4^{2-} and Cl^-), the other contained one ion (NH_4^+), were prepared and distributed to the laboratories. Blank filters, which were impregnated with K_2CO_3 or H_3PO_4 but did not contain any SO_4^{2-}, Cl^-, or NH_4^+, were also prepared and distributed. The details of the filter samples are described in Table 3.1. The analytical precision and accuracy on the individual analyte were summarized through statistical calculations of the submitted analytical results from each participating laboratory.

Table 3.1 Outline of filter samples

Name	Details	Container	Number of filters	Note
No.231d-1	Alkali (K_2CO_3) impregnated filter	Polyethylene centrifuge tube	3	Each filter contains a known quantity of sulfate and chloride ions.
No.231d-2	Acid (H_3PO_4) impregnated filter	Polyethylene centrifuge tube	3	Each filter contains a known quantity of ammonium ions.
No.232d-1	Alkali (K_2CO_3) impregnated filter	Polyethylene centrifuge tube	3	Each filter contains a known quantity of sulfate and chloride ions.

Table 3.1 Outline of filter samples (continued)

Name	Details	Container	Number of filters	Note
No.232d-2	Acid (H_3PO_4) impregnated filter	Polyethylene centrifuge tube	3	Each filter contains a known quantity of ammonium ions
No.233d-1	Alkali (K_2CO_3) impregnated filter	Polyethylene centrifuge tube	3	Blank
No.233d-2	Acid (H_3PO_4) impregnated filter	Polyethylene centrifuge tube	3	Blank

3.2.3 Analytes

All participating laboratories were expected to analyze these filter samples and to submit their values as the net quantity of each ion (SO_4^{2-}, Cl^- and NH_4^+) in microgram (µg).

3.2.4 Analytical Methodologies

The recommended procedure for sample analyses on the filter pack method is described in "*Technical Manual for Air Concentration Monitoring in East Asia*" (EANET, 2013). As each filter sample was put in a centrifuge tube, a solvent was directly poured into the tube for extraction. The extraction procedure is as follows;

(1) Sample No.231d-1, No.232d-1, No.233d-1

Add 20 mL of H_2O_2 solution (0.05% v/v) as an extracting solvent into each centrifuge tube, then shake them for 20 minutes.

(2) Sample No.231d-2, No.232d-2, No.233d-2

Add 20 mL of pure water (EC<0.15 mS m^{-1}) as an extracting solvent into each centrifuge tube, then shake them for 20 minutes.

(3) Filtration

Remove insoluble matter from the solution using a membrane filter (pore size 0.45 µm). The membrane filter must be prewashed with pure water (more than 100 mL) before filtration. After filtration, those filtrates are assigned identification numbers and sealed tightly.

> Note) In principle, it is strongly recommended that the filtrate be analyzed immediately after extraction, however, in the case that they need to be kept for certain reasons, store them in a refrigerator at 4ºC.

The participating laboratories were expected to use the analytical methods specified in *"Technical Manual for Wet Deposition Monitoring in East Asia – 2010"* (EANET, 2010) in Table 3.2.

Table 3.2 Analytical methods specified in the Technical Manual

Analyte	Analytical method
SO_4^{2-}, Cl^-	Ion Chromatography (preferably with suppressor) Spectrophotometry
NH_4^+	Ion Chromatography Spectrophotometry (Indophenol Blue)

3.2.5 Data Check Procedures

All participating laboratories were requested to report as the net quantity of each ion (SO_4^{2-}, Cl^- and NH_4^+) in the filter sample.
Each quantity (M_{sol}) is calculated as follows:

$$M_{sol} = C_{sol} \ x \ V_{sol} \qquad (1)$$

where M_{sol} : quantity of each component in the filtrate (μg);
C_{sol} : concentration of each component in the filtrate (mg L^{-1});
V_{sol} : volume of the solvent (20 mL)

The net quantity of each ion ($netM_{\mathrm{sol}}$) is calculated as follows:

$$net\,M_{\mathrm{sol}} = M_{\mathrm{sol,\,Sample}} - M_{\mathrm{sol,\,Blank}} \qquad (2)$$

where $netM_{\mathrm{sol}}$: net quantity of each ion on the filter;
$M_{\mathrm{sol,Sample}}$: quantity (μg) of each component in the filtrate from sample No.231d-1, No.231d-2, No.232d-1 and No.232d-2;
$M_{\mathrm{sol,Blank}}$: the median quantity (μg) in the filtrate from blank sample No.233d-1 and No.233d-2.

3.3 Results

The NC distributed the filter samples to 20 laboratories in the participating countries of EANET and received their results from 18 laboratories. The results compared to the prepared values are summarized in Table 3.3. The average, minimum, maximum, standard deviation (S.D.) and number of data (N) were calculated from each analyzed ion quantity. Outliers, defined as those results exceeding three standard deviations, excluded from the summary calculation shown in

Table 3.3 and 1 result was rejected this time.

As shown in Table 3.3, the deviations ($\Delta V/V\mathrm{p}$) for SO_4^{2-} in Sample No.231d and Sample No.232d were -11.7% and -3.7%. The deviations for Cl^- in Sample No.231d and Sample No.232d were -8.9% and -7.6%. The deviations for NH_4^+ in Sample No.231d and Sample No.232d were 0% and 0.7%.

The Data Quality Objectives (DQOs) of EANET are specified that determined values are expected to fall within ±15% deviation from the prepared values in *Technical Manual for Air Concentration Monitoring in East Asia* (2013). Each laboratory analyzed each sample 3 times, and these average values were evaluated based on the deviation from the corresponding prepared values. A flag "E" indicates that its deviation exceeds ±15% but not ±30%, and a flag "X" indicates that its deviation exceeds ± 30%.

$$\text{Deviation (\%)} = (\text{Determined value} - \text{Prepared value}) / \text{Prepared value} \times 100\ (\%) \qquad (3)$$

Flag E: $15\% < |\ \text{Deviation}\ | \leq 30\%$
Flag X: $30\% < |\ \text{Deviation}\ |$

The evaluation of the results on both Samples No.231d and No.232d is described in 3.3.1 Evaluation of Laboratories' Performance (by sample). The comparison of the results for each analyte is described in 3.3.2 Comparison of Laboratories' Performance (by analyte). The evaluation of their analytical circumstance, such as analytical method, experience of personnel, and other analytical conditions is described in 3.3.3 Information on Laboratories**.**

Table 3.3 Summary of analytical results of the filter samples

Analyte	Prepared* (Vp) (μg)	Average (Va) (μg)	$\Delta V/V$p* (%)	S.D. (μg)	Number (N)	Minimum (μg)	Maximum (μg)
Sample No.231d							
SO_4^{2-}	10.0	8.83	-11.7	1.23	18	6.35	11.0
Cl^-	5.02	4.58	-8.9	0.89	18	2.93	6.89
NH_4^+	18.1	18.1	0.0	3.73	17	9.25	25.4
Sample No.232d							
SO_4^{2-}	47.2	45.5	-3.7	2.87	18	38.2	49.3
Cl^-	15.1	14.0	-7.6	1.38	18	11.0	15.4
NH_4^+	50.3	50.7	0.7	2.62	16	46.0	54.3

* Prepared: Prepared values

* $\Delta V/V$p: (Average result (Va) − Prepared value (Vp)) / Prepared value (Vp) × 100 (%)

3.3.1 Evaluation of Laboratories' Performance (by sample)

Samples No.231d-1, No.231d-2

For Sample No.231d, 8 analytical data in 53 results were flagged E, and 8 analytical data were flagged X. The total percentage of the flagged samples was 32% (Figure 3.1, Table 3.4 and 3.5).

Table 3.4 Number of flagged data for Sample No.231d

	SO_4^{2-}	Cl^-	NH_4^+	Total
Flag E *	4	2	2	8
Flag X *	2	3	3	8
Data within DQOs	12	13	12	37
Ratio of Flagged (%)	33.3	27.8	29.4	30.2

*Flag E: 15% < | Deviation | ≤ 30%

*Flag X: 30% < | Deviation |

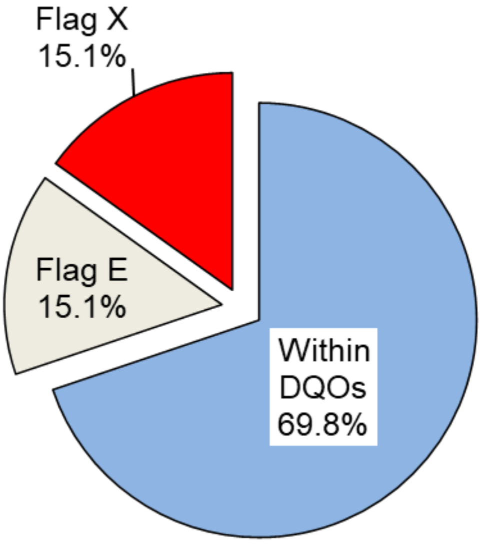


Figure 3.1 Percentage of flagged data for Sample No.231d

Table 3.5 Average analytical results of Sample No.231d

Lab. Code	SO$_4^{2-}$ (μg)		Cl$^-$ (μg)		NH$_4^+$ (μg)	
KH01*[1]	(9.00)		(3.31)	X	(14.8)	E
ID03	9.00		3.95	E	21.4	E
JP01	9.89		4.36		17.7	
JP02	10.1		4.62		19.1	
JP03	9.63		4.76		18.2	
JP04	9.57		4.62		18.2	
JP08	9.01		4.38		17.9	
JP09	9.53		4.85		18.9	
JP10	9.63		4.82		17.3	
LA01	9.39		5.20		18.9	
MY01	9.41		4.64		17.7	
MN01	10.5		5.08		25.4	X
MM01	6.35	X	5.68		18.2	
PH01	9.00		3.57	E	18.9	
KR01	7.91	E	6.89	X	21.2	E
TH01	6.48	X	4.57			
TH02	8.00	E	4.45		20.1	
VN01	7.55	E	2.99	X	9.39	X
VN03	7.45	E	2.93	X	9.25	X

Note: Flag E: 15% < | Deviation | ≤ 30%

Flag X: 30% < | Deviation |

*1: KH01 results were treated as reference values, since they were submitted after the prepared values were disclosed. They were not included in their compilation.

Samples No.232d-1, No.232d-2

For Sample No.232d, 4 analytical data in 53 results were flagged E, and 1 analytical dat were flagged X. The total percentage of the flagged samples was 9.4% (Figure 3.2, Table 3.6 and 3.7).

Table 3.6 Number of flagged data for Sample No.232d

	SO_4^{2-}	Cl^-	NH_4^+	Total
Flag E *	1	3	0	4
Flag X *	0	0	1	1
Data within DQOs	4	2	2	8
Ratio of Flagged (%)	5.6	16.7	5.9	9.4

*Flag E: 15% < | Deviation | ≤ 30%

*Flag X: 30% < | Deviation |

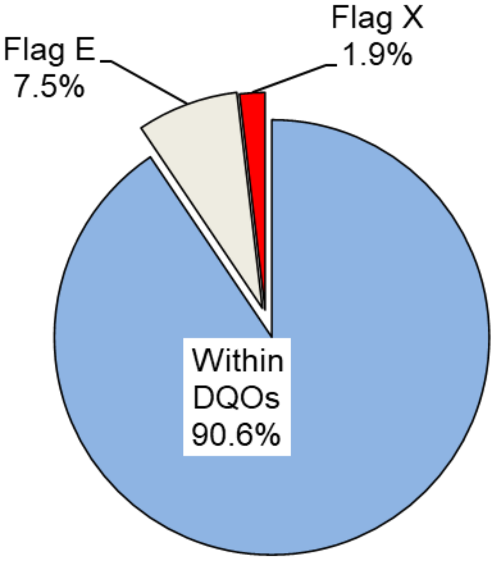


Figure 3.2 Percentage of flagged data for Sample No.232d

Table 3.7 Average analytical results of Sample No.232d

Lab. Code	SO_4^{2-} (µg)	Cl^- (µg)	NH_4^+ (µg)
KH01*[1]	(41.6)	(10.9) E	(59.0) E
ID03	47.9	12.9	54.3

JP01	46.7		14.9		47.8	
JP02	46.5		14.6		54.3	
JP03	47.2		14.7		49.1	
JP04	46.6		14.5		50.0	
JP08	44.3		14.1		50.3	
JP09	45.9		14.8		48.8	
JP10	47.2		14.9		49.3	
LA01	46.5		11.2	E	50.6	
MY01	44.5		14.5		52.2	
MN01	47.9		15.2		70.0	X
MM01	38.2	E	14.7		53.1	
PH01	42.1		13.6		52.0	
KR01	43.8		15.4		53.0	
TH01	40.5		14.6			
TH02	43.9		14.4		53.6	
VN01	49.3		11.0	E	46.0	
VN03	49.2		11.2	E	46.1	

Note: Flag E: 15% < | Deviation | ≤ 30%

Flag X: 30% < | Deviation |

*1: KH01 results were treated as reference values, since they were submitted after the prepared values were disclosed. They were not included in their compilation.

Blank Sample (No.233d)

Each quantity of SO_4^{2-}, Cl^-, and NH_4^+ was determined for blank sample No.233d-1 and No.233d-2. Their obtained values are shown in Table 3.8. Blank values were detected in a wide range, including 0 μg.

Table 3.8 Analytical results of Blank Sample No.233d

Lab. Code	SO_4^{2-} (μg)	Cl^- (μg)	NH_4^+ (μg)
KH01*[1]	(7.70)	(12.9)	(4.12)
ID03	0.65	1.74	0.37
JP01	0	0.77	0.04
JP02	0	1.05	0.58
JP03	0	1.22	0.66
JP04	0.51	1.29	0.28
JP08	0.44	1.50	0.04

JP09	0	1.00	0.67
JP10	0.16	1.13	0.49
LA01	2.32	1.00	0.25
MY01	0.25	1.36	0.14
MN01	0.04	1.35	0.69
MM01	0.04	2.71	0.69
PH01	0.29	2.94	0
KR01	0.25	1.53	0.62
TH01	1.04	2.16	
TH02	0.50	2.06	0.75
VN01	0.92	1.04	1.02
VN03	1.09	1.21	1.06
Average	0.47	1.50	0.49
Median	0.27	1.32	0.58
Minimum	0.00	0.77	0.00
Maximum	2.32	2.94	1.06
Standard deviation	0.57	0.58	0.32

*1: KH01 results were treated as reference values, since they were submitted after the prepared values were disclosed. They were not included in their compilation and statistics.

3.3.2 Comparison of Laboratories' Performance (by analyte)

The overviews of their results are shown in the following figures and tables for each analyte (SO_4^{2-}, Cl^- and NH_4^+). The obtained values from each laboratory were evaluated for their deviations. The number of the flagged data is shown in Table 3.9, 3.10 and 3.11 for each analyte.

SO_4^{2-} (Sulfate)

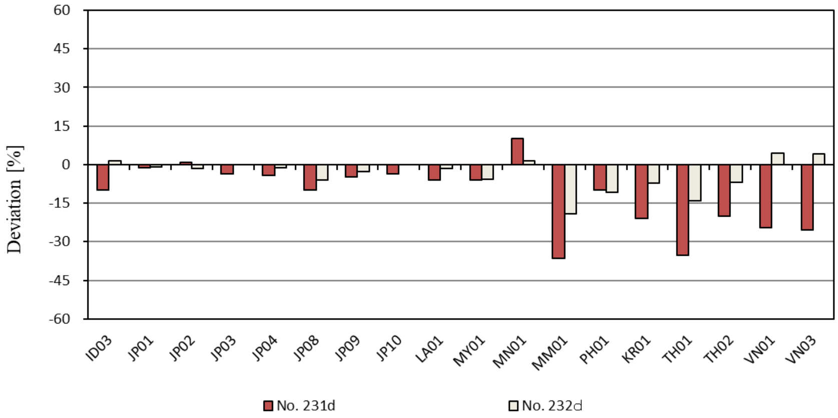


Figure 3.3 Deviation for SO_4^{2-}

Deviation (%) = (Determined value - Prepared value) / Prepared value × 100 (%)

Table 3.9 Flagged data of SO_4^{2-}

	Flag E	Flag X	Flagged (%)
Sample No.231d	4	2	33.3
Sample No.232d	1	0	5.6

All laboratories used Ion Chromatography for the determination of SO_4^{2-}. E flag appeared at 5 laboratories for Sample No.231d and No.232d. X flag appeared at 2 laboratories for Sample No.231d.

Cl^- (Chloride)

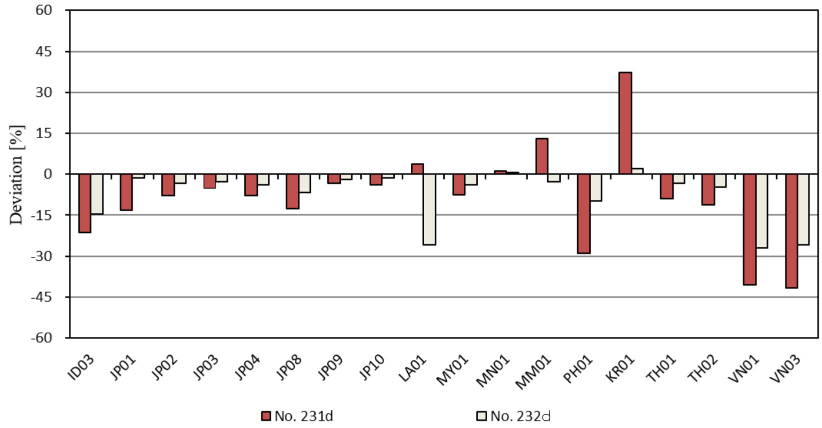


Figure 3.4 Deviation for Cl^-

Table 3.10 Flagged data of Cl$^-$

	Flag E	Flag X	Flagged (%)
Sample No.231d	2	3	27.8
Sample No.232d	3	0	16.7

As with the analysis of Cl$^-$, all laboratories used Ion Chromatography for the determination of Cl$^-$. E flag appeared at 5 laboratories for Sample No.231d and No.232d. X flag appeared at 3 laboratories for Sample No.231d.

NH$_4^+$ (Ammonium)

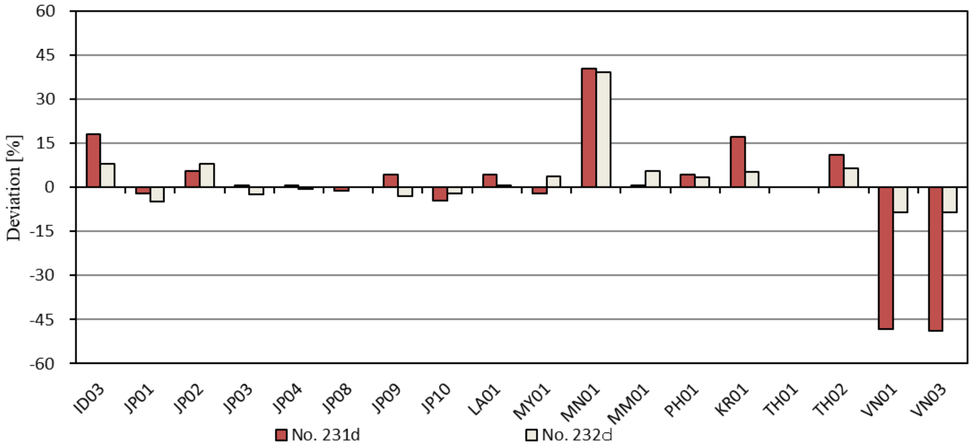


Figure 3.5 Deviation for NH$_4^+$

Table 3.11 Flagged data of NH$_4^+$

	Flag E	Flag X	Flagged (%)
Sample No.231d	2	3	29.4
Sample No.232d	0	1	5.9

One laboratory used the spectrophotometry method. The other laboratories used Ion Chromatography for the determination of NH$_4^+$. E flag appeared at 2 laboratories for Sample No.231d. X flag appeared at 4 laboratories for No.231d and No.232d.

3.3.3 Information on Laboratories

Years of staff experience

Years of staff experience are summarized in Table 3.12. A light gray color cell indicates that there is a flag for Sample No.231d or No.232d. A dark gray color cell indicates the flagged data in both Sample No.231d and No.232d.

Table 3.12 Years of staff experience

Lab. Code	SO_4^{2-}	Cl^-	NH_4^+
KH01*[1]	(1)	▓ (1)	▓ (1)
ID03	15	░ 15	░ 15
JP01	20	20	20
JP02	4	4	4
JP03	2	2	2
JP04	6	6	6
JP08	2	2	2
JP09	9	9	9
JP10	4	4	4
LA01	4	░ 4	4
MY01	5	5	5
MN01	20	20	▓ 20
MM01	▓ 2	2	2
PH01	2	2	2
PH02			
KR01	░ 18	18	░ 18
TH01	░ 1	1	
TH02	░ 25	25	25
VN01	░ 10	░ 10	░ 10
VN03	░ 10	░ 10	░ 10

░ : One sample is flagged.

▓ : Two samples are flagged.

*1: KH01 results were treated as reference values, since they were submitted after the prepared values were disclosed. They were not included in their compilation and statistics.

Flagged Data

In the results of Sample No.231d and No.232d, the total number of the flagged data was 21 (E: 12, X: 9) in the whole values (108). The number of the flagged data in each laboratory is shown in Figure 3.6. Eight laboratories met DQOs (42.1%).

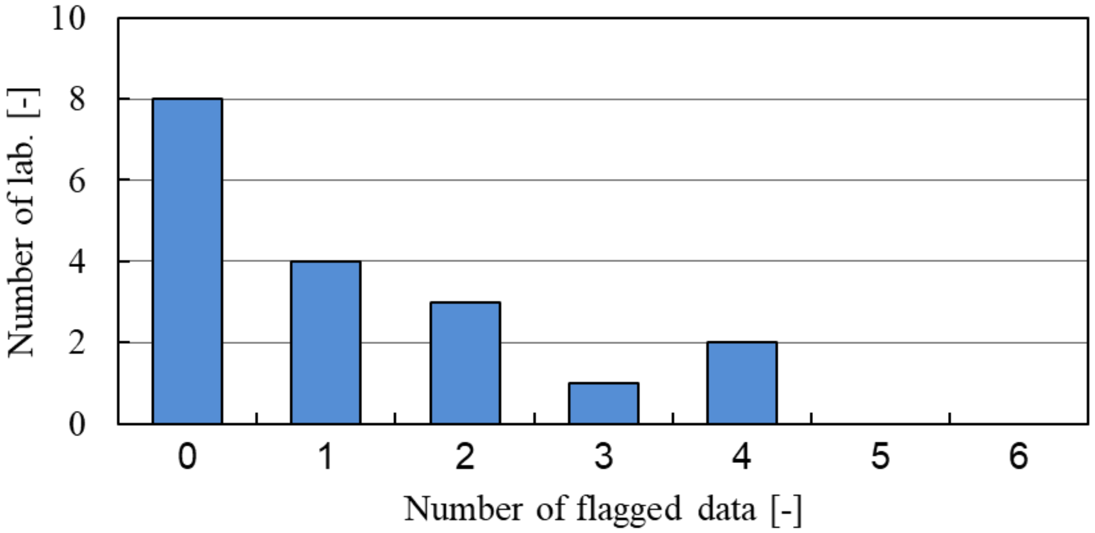


Figure 3.6 Number of flagged data and laboratories

Calibration standard solution

The ranges of the calibration standard solution in each laboratory are shown in Figure 3.7 with the prepared values and their laboratory results, which were converted in µmol L^{-1}. Each concentration of the prepared values was expected within the range of both concentrations of lowest and highest standard solutions. If the concentrations of their obtained values were not in the range of the calibration standard, laboratories should have analyzed again with the appropriate concentration range of standard solution.

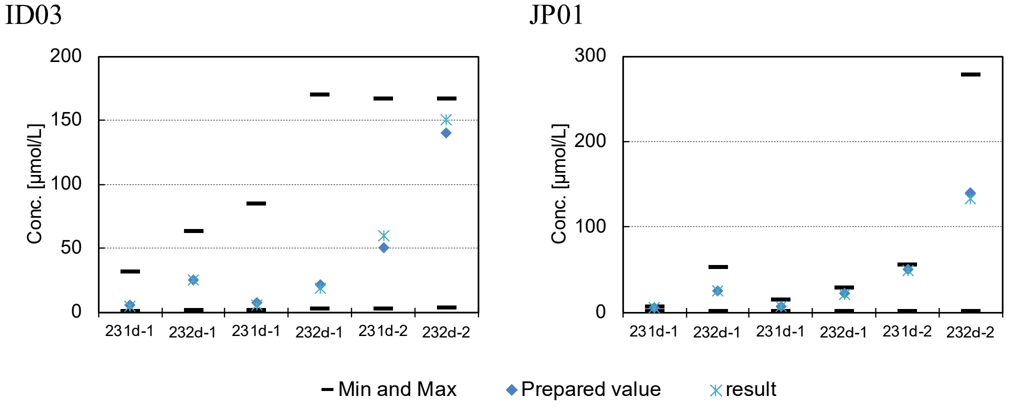


Figure 3.7 Ranges of the calibration standard solution in each laboratory

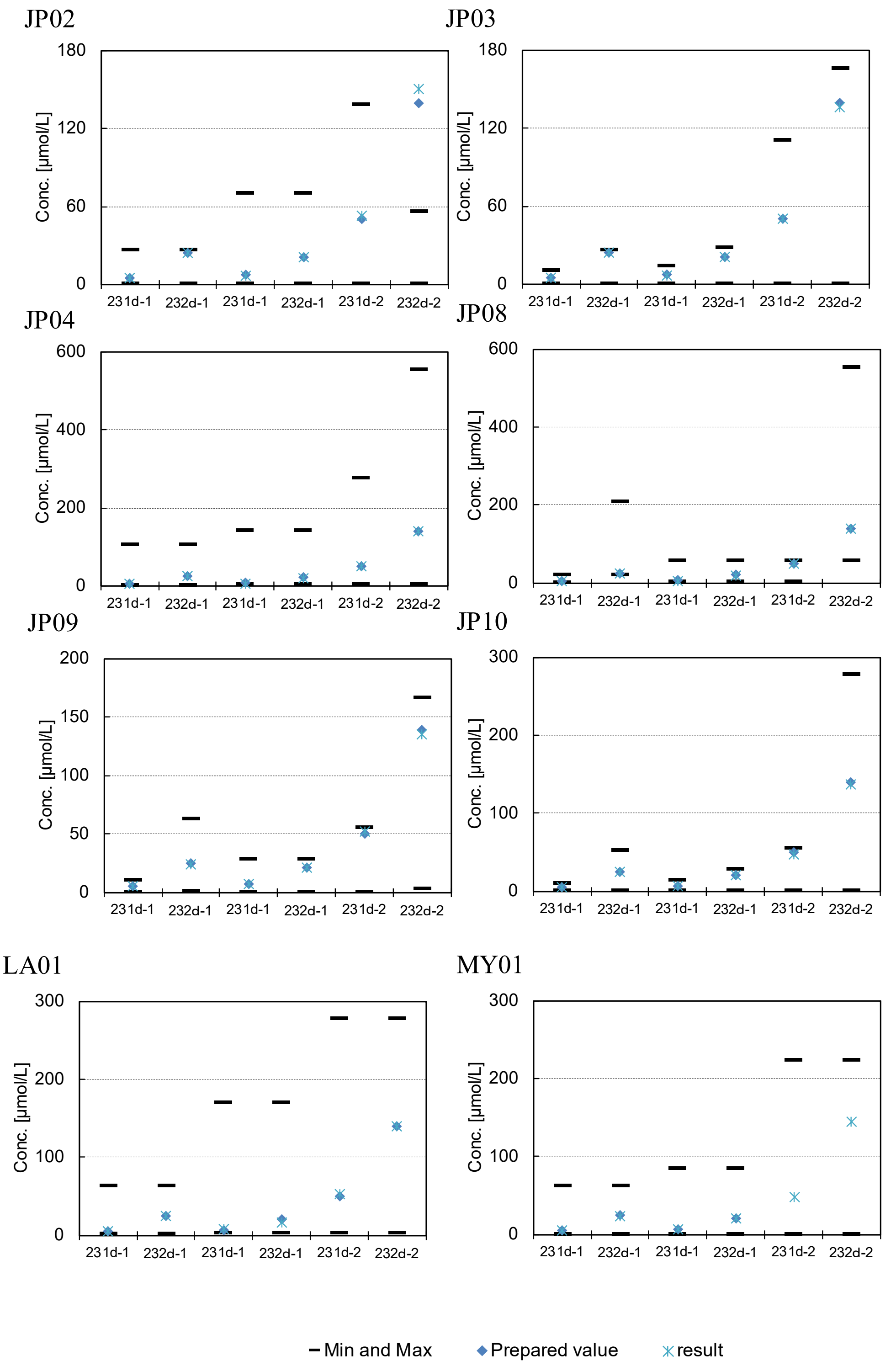


Figure 3.7 Ranges of the calibration standard solution in each laboratory (continued)

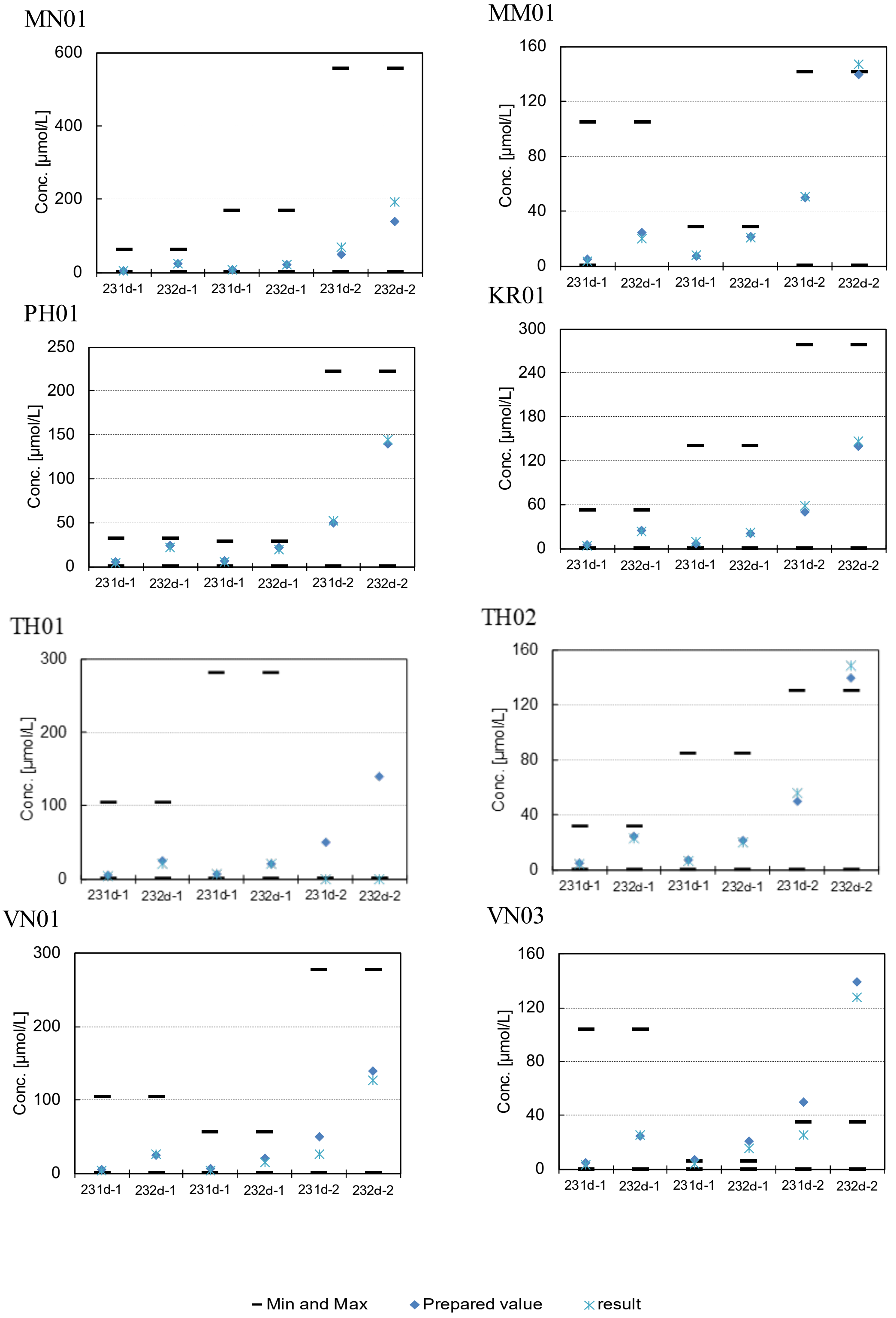


Figure 3.7 Ranges of the calibration standard solution in each laboratory (continued)

3.4 Comparison with past surveys

This Inter-laboratory Comparison on dry deposition has been implemented since 2005. The results showing the percentages of flagged data and percentages of data that were satisfied the DQOs were shown in Figure 3.8.

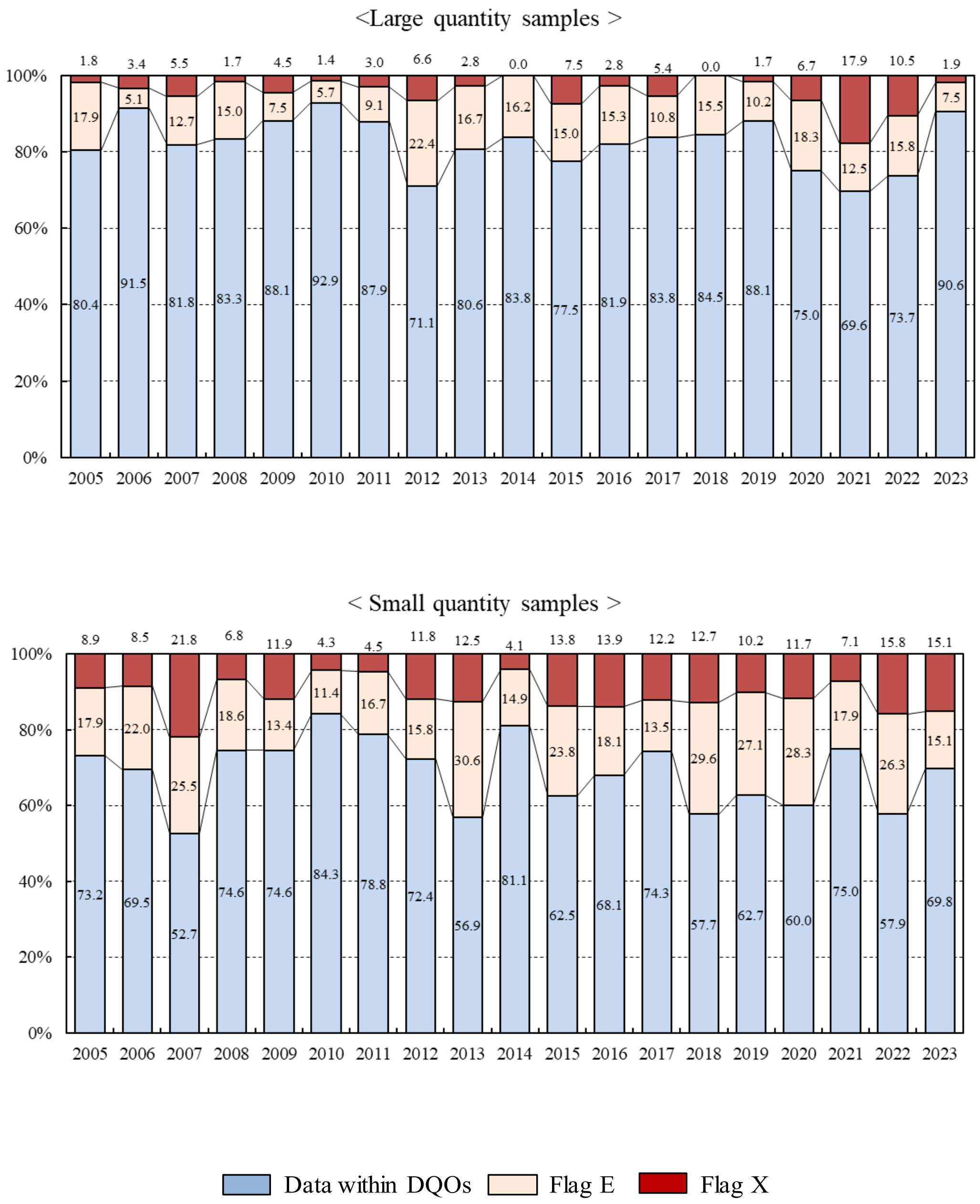


Figure 3.8 Comparison of DQOs' results for the past years

The comparison for each analyte in Inter-laboratory Comparison on dry deposition year–by-year is shown in Figure 3.9.

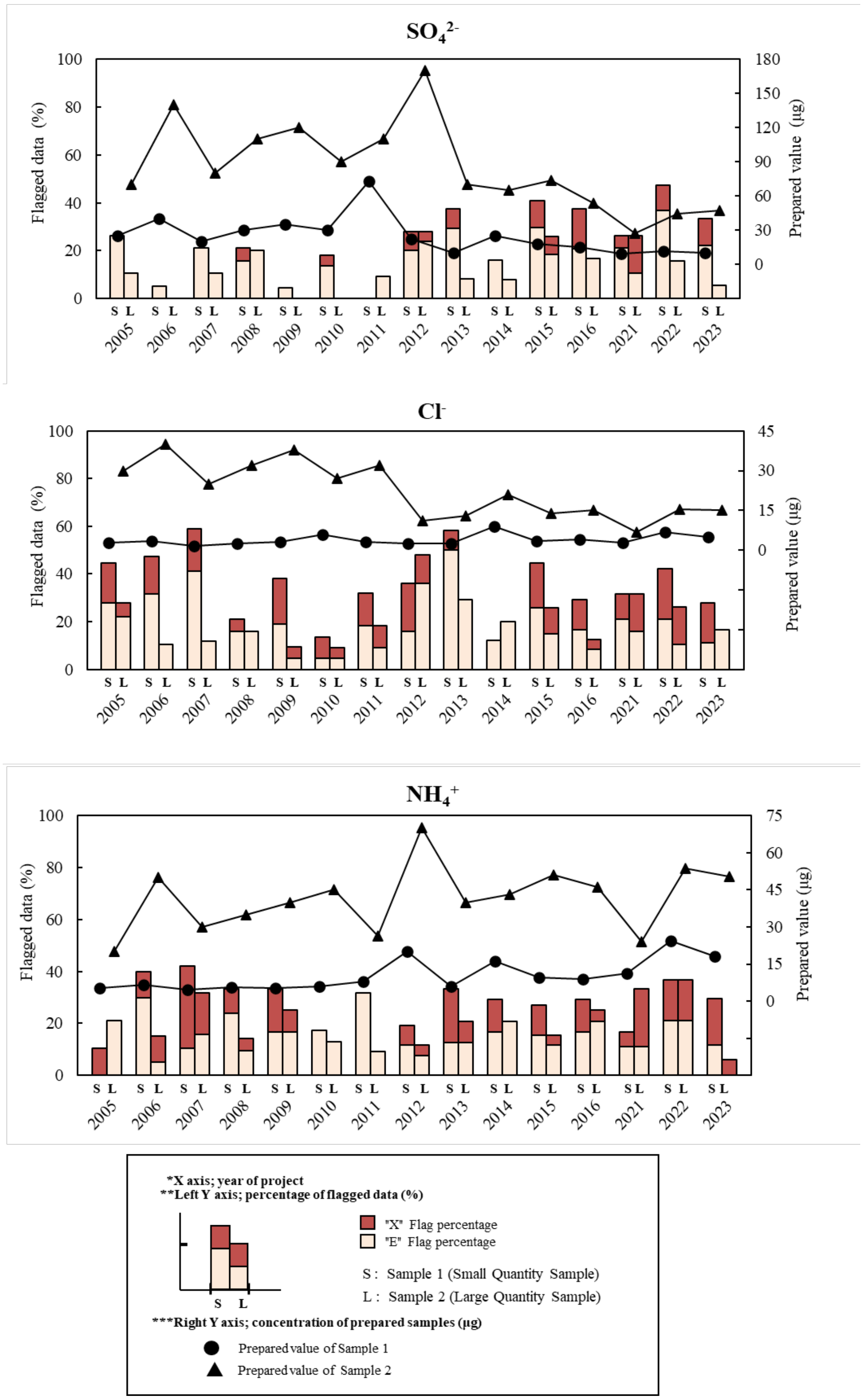


Figure 3.9 Comparison for each parameter in Inter-laboratory comparison project

3.5 Recommendations for improvement

Filter samples are put in centrifuge tubes, and then the extracting solvents are directly added into the tubes. The extraction and filtration procedures are specified in the "Technical Manual for Air Concentration Monitoring in East Asia, December 2013"

3.5.1 Measurement and Analyses

► Before setting a shaker and start shaking for 20 minutes, shake each tube by hand sufficiently.

► Samples should not be diluted even though the concentration of the analytical sample exceeds that of the highest standard solution you prepared. Instead, add one or two higher standard solutions during analyses and measure its values within the calibration curve range.

► Extraction, filtration, and analyses should be done on the same day once you open the bag. In particular, special care for NH_4^+ determination. (Be aware that sample solutions may be contaminated by ammonia in a laboratory. Even each sample sets in an autosampler with a cap may be possibly contaminated by ammonia during analyses.)

► It is strongly recommended that only the interlaboratory samples should be analyzed in sequence to minimize contamination during analyses. Regular samples should not be analyzed simultaneously with the interlaboratory samples.

References

EANET (2010). *Technical Manual for Wet Deposition Monitoring in East Asia-2010*. Asia Center for Air Pollution Research, Niigata, Japan, 113p.

EANET (2013). *Technical Manual for Air Concentration Monitoring in East Asia*. Asia Center for Air Pollution Research, Niigata, Japan, 155p.

4. 25th INTER-LABORATORY COMPARISON PROJECT ON SOIL

4.1 Introduction

The Inter-Laboratory Comparison Project on Soil started in 1999 as one of the activities within the QA/QC program on Soil and Vegetation Monitoring. The project will clarify inter-laboratory precision as well as within-laboratory and repeatability precision to improve the analytical quality of the EANET laboratories. Possible factors affecting precisions have been discussed in previous projects.

Soil analysis has complicated procedures and steps in comparison with environmental water. Steps in the procedures of soil analysis may be related to the variation among laboratories, e.g., extraction, instrumental analysis, and/or titration. Results of the first three projects from 1999 to 2001 suggested that instrumental analysis has a relatively large effect on the total precision of soil analysis. Additionally, the following analytical conditions could affect results:

- Addition of La or Sr solution for AAS analysis of Ex-Ca and Ex-Mg.
- Preparation method of standard solution.
- Instrument for Ex-K and Na analysis.

The participating laboratories shared information on these potential factors to improve precision.

The 25th project involved the Network Center (NC) providing two soil samples (No.231s and No.232s) to laboratories to standardize methods and improve inter-laboratory precision. The data from participating laboratories were statistically evaluated according to the QA/QC program for soil monitoring. These results may help assess inter-laboratory variation in soil monitoring and provide useful insights for enhancing the precision of soil analysis within EANET.

4.2 Procedures

4.2.1 Participating Laboratories

Eight laboratories from four countries participated in the 25th project. The results submitted were statistically analyzed by the NC as part of the QA/QC program. The names of the participating laboratories are listed in Table 1.1.

4.2.2 Description of Samples

The characteristics of the soil samples are as follows:

Sample No.231s: Cambisols
Sample No.232s: Cambisols

Soil samples of No.231s and No.232s were collected under Japanese larch (*Larix kaempferi*) and Japanese cedar (*Cryptomeria japonica*), respectively, in Toyama Prefecture, Japan. Both samples were collected from the B-horizon, primarily composed of mineral soil. The soils were air-dried, sieved to obtain particles smaller than 2 mm (i.e., particles smaller than 2 mm, also known as fine soil), and thoroughly mixed through a series of procedures. This included dividing the bulk sample into two parts, mixing each part, recombining them, and repeating the process fifteen times to ensure complete homogeneity. Finally, portions of 400-500 g were weighed out, packed into 500 mL plastic bottles, and sterilized using radioisotopes (50 kGy) for distribution to participating countries.

4.2.3 Parameters Analyzed

All the participating laboratories were expected to measure the parameters shown in Table 4.1.

Table 4.1 Parameters to be measured

Parameters	Unit	Mandatory or not
a) Moisture Content	wt %	M
b) pH(H_2O)	-	M
c) pH(KCl)	-	M
d) Exchangeable Ca^{2+}	$cmol_c\ kg^{-1}$	M
e) Exchangeable Mg^{2+}	$cmol_c\ kg^{-1}$	M
f) Exchangeable K^+	$cmol_c\ kg^{-1}$	M
g) Exchangeable Na^+	$cmol_c\ kg^{-1}$	M
h) Exchangeable acidity	$cmol_c\ kg^{-1}$	M
i) Exchangeable Al^{3+}	$cmol_c\ kg^{-1}$	M
j) Exchangeable H^+	$cmol_c\ kg^{-1}$	M

M: Mandatory items

“Exchangeable” were abbreviated to “Ex-”in this report; e.g., Ex-Ca, Ex-Mg, etc.

4.2.4 Analytical Methodologies

All procedures for chemical analysis were carried out according to the “Technical Manual for Soil and Vegetation Monitoring in East Asia” (EANET, 2000). In each laboratory, all parameters were analyzed three times under identical conditions (same analyst, time, and instrument). Subsequently, the analytical procedures were repeated twice under within-laboratory reproducibility conditions, with different analysts, times, and instruments.

4.2.4.1 Standardization of methods

All procedures for chemical analysis should be carried out in accordance with the "Technical Documents for Soil and Vegetation Monitoring in East Asia (March 2000, Adopted at: The Second Interim Scientific Advisory Group Meeting of Acid Deposition Monitoring Network in East Asia)". Furthermore, the following analytical procedures have been standardized:

(1) **Atomic absorption spectrometry (AAS)** should be used for the analysis of Ex-Ca, Mg, K, and Na. If AAS cannot be used, Flame (emission) photometry method is acceptable for Ex-K and Na.
(2) **Titration method** should be used for the analysis of Ex-acidity, Al, and H.
(3) **Calibration curve method** should be used for the determination of Ex-Ca, Mg, K, and Na.
(4) The samples should be extracted and diluted with **1 M CH_3COONH_4 (pH 7.0)** for the analysis of Ex-Ca, Mg, K, and Na. Then, 1 M CH_3COONH_4 (pH 7.0) solution should be used to prepare each standard solution as the solvent.
(5) **Sr** solution should be added to the samples and each standard solution to eliminate the interference of the sample for analysis of Ex-Ca and Mg. If Sr is not available, La is acceptable.

4.2.4.2 Procedures for Ex-base cations

(1) Extract from air-dry sample with 1 M CH_3COONH_4 (pH 7.0) solution.
(2) Pipette an appropriate aliquot of the soil extract into a volumetric flask and add 100 g-Sr L^{-1} solution to achieve a final concentration of 1000 mg-Sr L^{-1} ($SrCl_2$ solution eliminates interference from the sample). Then, bring to volume with 1 M CH_3COONH_4 (pH 7.0). This solution is named "Prepared sample".
(3) Prepare three "prepared samples".
(4) Prepare each standard solution by diluting 1 M CH_3COONH_4 (pH 7.0) solution.
(5) Add 100 g-Sr L^{-1} solution to each standard solution to achieve the same concentration of $SrCl_2$ as in the sample.
(6) Analyze the standard solution and the prepared samples by AAS.
(7) Store the calibration curves securely and report them together with the reporting formats.
(8) Repeat steps 1) - 7) twice.
(9) Calculation of content in the soil

Content in the soil can be calculated using the following formulas:

$$\text{Ex-Ca (cmol}_c\text{ kg}^{-1}\text{ soil)} = [A \times B \times V \times mcf] / [10 \times 20.04 \times S]$$

$$\text{Ex-Mg (cmol}_c\text{ kg}^{-1}\text{ soil)} = [A \times B \times V \times mcf] / [10 \times 12.15 \times S]$$

$$\text{Ex-K (cmol}_c\text{ kg}^{-1}\text{ soil)} = [A \times B \times V \times mcf] / [10 \times 39.10 \times S]$$

$$\text{Ex-Na (cmol}_c\text{ kg}^{-1}\text{ soil)} = [A \times B \times V \times mcf] / [10 \times 23.00 \times S]$$

where,

A = Measurement values of prepared (diluted) samples (mg L^{-1})
B = Dilution ratio (B = 2, if 25 mL sample was diluted to 50 mL for making prepared sample.)
mcf = Moisture correction factor (Measured value)
S = Weight of air-dry sample (g)
V = Volume of extract (mL)

4.2.4.3 Procedures for Ex-acidity

(1) Extraction and titration should be carried out according to the "Technical Documents for Soil and Vegetation Monitoring in East Asia".
(2) Prepare three samples and analyze each sample along with at least one blank.
(3) Repeat the procedure twice.
(4) Calculation of content in the soil:
Content in the soil can be calculated using the following formulas:

$$\text{Ex-acidity (cmol}_c\text{ kg}^{-1}\text{ soil)} = [(A_{\mathrm{NaOH}} - bl_{\mathrm{NaOH}}) \times M_{\mathrm{NaOH}} \times c \times 100 \times mcf] / S$$

$$\text{Ex-Al (cmol}_c\text{ kg}^{-1}\text{ soil)} = [(A_{\mathrm{HCl}} - bl_{\mathrm{HCl}}) \times M_{\mathrm{HCl}} \times c \times 100 \times mcf] / S$$

$$\text{Ex-H (cmol}_c\text{ kg}^{-1}\text{ soil)} = [\{(A_{\mathrm{NaOH}} - bl_{\mathrm{NaOH}}) \times M_{\mathrm{NaOH}} - (A_{\mathrm{HCl}} - bl_{\mathrm{HCl}}) \times M_{\mathrm{HCl}}\} \times c \times 100 \times mcf] / S$$

where,

A_{NaOH} = Titration volume of 0.025 M NaOH solution needed for percolate (mL)
A_{HCl} = Titration volume of 0.02 M HCl solution needed for percolate (mL)
bl_{NaOH} = Titration volume of 0.025 M NaOH solution needed for blank (mL)
bl_{HCl} = Titration volume of 0.02 M HCl solution needed for blank (mL)
M_{NaOH} = Molarity of NaOH solution (mol L^{-1})
M_{HCl} = Molarity of HCl solution (mol L^{-1})
S = Weight of air-dry sample (g)
c = Aliquot factor (c = 2, if 50 mL percolate of 100 mL is used.)

4.2.4.4 Detection limit and quantification limit for Ex-base cation analysis

From the 21^{st} project, it was recommended to report detection limit and quantification limit for Ex-base cations. Generally, these limit values are calculated as follows.

(1) A standard solution with the lowest concentration (Std-1 [mg L^{-1}]) should be measured for more than 5 times, and standard deviation (s.d.) of the Std-1 should be calculated.
(2) The detection limit and quantification limit are calculated from the respective formulae as follows:
Detection limit = 3*(s.d.) [mg L^{-1}]
Quantification limit = 10*(s.d.) [mg L^{-1}]

4.2.4.5 Reporting

(1) Report preparation

Participating laboratories are provided with digital formats (Microsoft Excel), which automatically calculate the chemical properties of soil samples based on the formulas in the formats.

(2) Report submission

Entered data in digital formats, along with other information such as calibration curves, are submitted via email.

4.2.4.6 Data Checking Procedures

We statistically evaluated the data according to the following procedures described in the "Technical Manual for Soil and Vegetation Monitoring in East Asia" (2^{nd} ISAG, 2000). Dataset with one decimal place for pH and two decimal places for Ex-cation concentrations and Ex-acidity were used for the statistical analysis.

1) General description of the data variability

Mean, median, variance and coefficient variation (CV) were calculated for the entire dataset in the inter-laboratory project. Box-and-whisker plots were also used to check the data variability and detect outliers in the dataset visually.

2) Detection of outliers to prepare the verified dataset

The evenness of within-laboratory precision (variation in each laboratory) and inter-laboratory precision (variation between 8 laboratories) were verified by Cochran and Grubbs methods, respectively. We also computed "verified" mean, median and other statistical summaries from verified datasets. In the inter-laboratory comparison project on soil, the "verified" mean will be a good reference to assess the analyzed value of each laboratory.

3) Analysis of variance

Total variation among laboratories includes within-laboratory and inter-laboratory variations. As described in the following equation, the total sum of square (S_T) consists of the sum of square inter-laboratories (S_R), sum of square within-laboratory (S_{RW}), and sum of square repeatability (S_r).

$$S_T = S_R + S_{RW} + S_r$$

Based on the above equation, inter-laboratories variance, within-laboratory-reproducibility variance, and repeatability variance were calculated, and then the precision was estimated.

4) Calculation of permissible tolerance

Permissible tolerances were calculated based on the above precision: 1) repeatability limit, 2) within-laboratory reproducibility limit, and 3) inter-laboratory reproducibility limit. Permissible tolerances are meaningful to determine "5% significant difference" in actual monitoring data. For instance, significantly temporal changes in the same site or significant difference between two laboratories would be indicated if those changes or the difference were more than “within-laboratory reproducibility limit” or “inter-laboratory reproducibility limit”.

4.3 Results

4.3.1 General description of the data variability

The statistical summary is shown in Table 4.2. In the 25th inter-laboratory project, Ex-Ca and Ex-Mg concentrations in 231s were lower than those in 232s, and Ex-acidity and Ex-Al concentrations in 231s were higher than those in 232s. We observed large variations in the analyzed data (CVs) of Ex-base cations (approx. 7-70%), Ex-acidity (25-30%), and acid cations (20-170%) in both samples. Meanwhile, in both samples, CVs were relatively small for both pH(H_2O) and pH(KCl) (< 4%).

Table 4.2 Basic statistics of the entire dataset

Statistics	pH(H_2O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
			$cmol_c\ kg^{-1}$						
	No. 231s								
Number of Laboratories	8	8	5	5	5	5	7	7	7
Total average	4.6	4.2	0.19	0.11	0.15	0.07	3.71	3.47	0.91
Median	4.6	4.1	0.22	0.07	0.16	0.07	3.72	3.51	0.42
Maximum	4.9	4.3	0.31	0.18	0.17	0.11	5.18	4.75	4.49
Minimum	4.3	4.1	0.04	0.06	0.11	0.02	2.06	1.93	0.13
Standard deviation	0.2	0.1	0.13	0.06	0.03	0.03	0.93	0.84	1.59
CV (%)*1	3.4	2.0	68.8	56.6	20.0	49.5	24.9	24.1	174.0
	No. 232s								
Number of Laboratories	8	8	5	5	5	5	7	7	7
Total average	4.9	4.1	2.03	0.43	0.10	0.07	1.99	1.70	0.68
Median	5.0	4.1	2.11	0.42	0.11	0.07	2.21	1.90	0.40
Maximum	5.1	4.3	2.16	0.53	0.11	0.08	2.47	2.04	2.52
Minimum	4.6	4.0	1.81	0.34	0.09	0.03	0.74	0.70	0.04
Standard deviation	0.1	0.1	0.15	0.08	0.01	0.02	0.58	0.47	0.84
CV (%)*1	3.0	2.5	7.6	19.5	9.5	29.1	29.2	27.8	123.9

*1: CV, Coefficient of variance (%) = (standard deviation/average)*100

We also have an overview of the data by box-and-whisker plot (Figure 4.1) of No.231s and 232s analyzed by 8 laboratories. The box-and-whisker plot provides the six-number summaries: the total average shown by an open diamond, lower quartile, median, and upper quartile shown by a box and a bold line, and the lowest and highest values drawn by error bars representing the range between the lower quartile minus 1.5 times the inter-quartile range and the upper quartile plus 1.5 times the inter-quartile range. Additionally, values outside the error bars are shown as outliers, which are considered non-parametric outliers. The plots showed several non-parametric outliers in each item. These outliers might be due to incorrect calculations, procedures, irregular contamination, and so on. Therefore, in the following section, we removed these outliers using a parametric statistical method to calculate a reference closer to the true value.

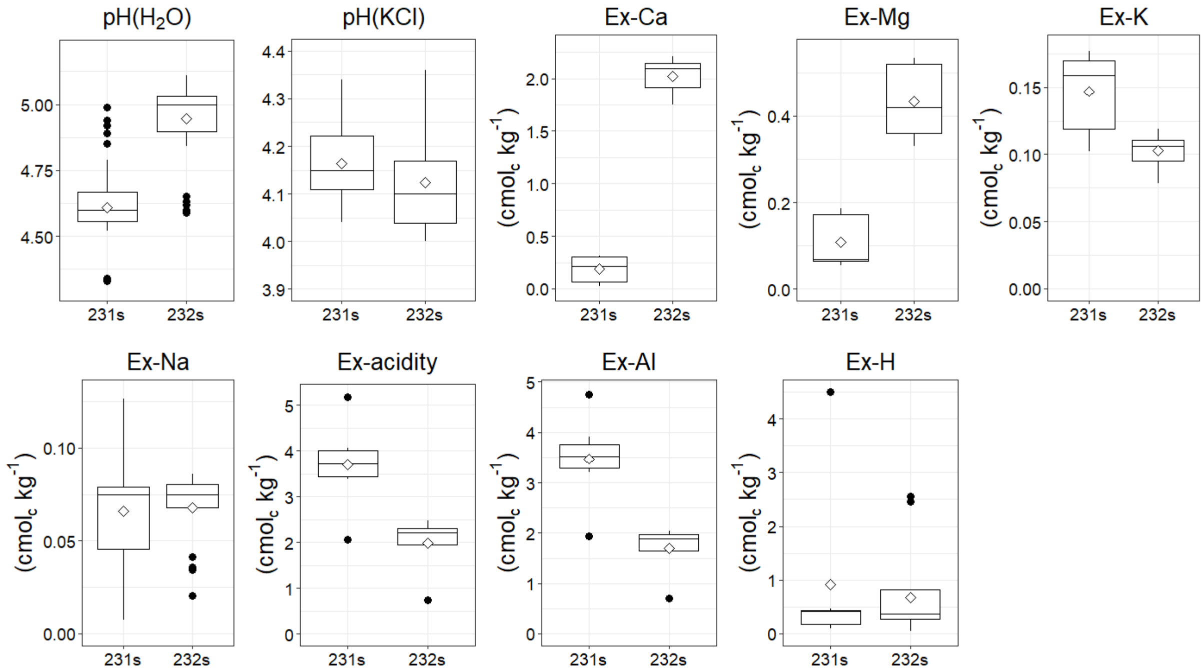


Figure 4.1 Data variability of No.231s and No.232s

4.3.2 Detection of outliers

Detection of outliers by the Cochran-Grubbs test is shown in Table 4.3. Laboratories exhibiting significantly large differences in repeat analyses, as determined by the Cochran test (examining the evenness of within-laboratory precision), were identified as outliers. For example, the “c” sign was observed for “MN01” in pH(H_2O) of No.231s. Subsequently, the remaining data were tested using the Grubbs test (examining the average value of each laboratory). In this test, laboratories with significantly large or small averages were identified as outliers. For instance, the “g” sign was observed for “ID01” in pH(H_2O) of No. 231s. The Cochran-Grubbs test detected several outliers for each item. After removing these outliers, the “verified” dataset consisting of 5-7 laboratories for pH(H_2O) and pH(KCl), 4-5 laboratories for Ex-base cations, and 5-7 laboratories in Ex-acidity, Al, and H was used for further analysis in the following section (Table 4.4).

Table 4.3 Data verification by Cochran-Grubbs tests
No. 231s

Country	Lab.	Repeat analysis	$pH(H_2O)$	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
								$cmol_c\ kg^{-1}$			
Indonesia	ID01	1st	4.3 g	4.0	0.07	0.06	0.16	0.05	2.06	1.93	0.13
		2nd	4.3 g	4.1	0.07	0.06	0.16	0.05	2.06	1.93	0.13
	ID04	1st	4.6	4.2	0.22	0.06	0.12	0.11	3.40	3.27	0.13 c
		2nd	4.6	4.2	0.21	0.06	0.13	0.11	3.42	3.25	0.17 c
Mongolia	MN01	1st	4.9 c	4.3	NA	NA	NA	NA	5.18	4.75	0.43
		2nd	4.9 c	4.3	NA	NA	NA	NA	5.18	4.75	0.43
Philippines	PH01	1st	4.6 c	4.1 c	0.04	0.07	0.11	0.02	3.66	3.83	0.32
		2nd	4.5 c	4.2 c	0.03	0.07	0.11	0.02	3.65	3.78	0.31
Vietnam	VN01	1st	4.6	4.2	0.30	0.17	0.17	0.08	3.92	3.46 c	0.42
		2nd	4.6	4.1	0.31	0.17	0.17	0.08	3.91	3.56 c	0.42
	VN02	1st	4.6	4.1	NA	NA	NA	NA	4.05	3.60	4.49 g
		2nd	4.6	4.1	NA	NA	NA	NA	4.05	3.60	4.49 g
	VN04	1st	4.7	4.2	0.31	0.18	0.17	0.07	3.72	3.44	0.43
		2nd	4.7	4.2	0.31	0.18	0.17	0.08	3.72	3.44	0.43
	VN05	1st	4.6	4.1	NA	NA	NA	NA	NA	NA	NA
		2nd	4.6	4.1	NA	NA	NA	NA	NA	NA	NA

The outliers were determined by Cochran and Grubbs tests, and were indicated by "c" and "g" signs, respectively.

Table 4.3 Data verification by Cochran-Grubbs tests (continued)
No. 232s

Country	Lab.	Repeat analysis	$pH(H_2O)$	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
								$cmol_c\ kg^{-1}$			
Indonesia	ID01	1st	5.0	4.1	1.94	0.36	0.11	0.07	0.74 g	0.70 g	0.04
		2nd	5.0	4.1	1.90	0.36	0.11	0.07	0.74 g	0.70 g	0.04
	ID04	1st	5.0	4.2	2.18	0.34	0.09	0.07	1.98	1.63	0.36
		2nd	5.0	4.2	2.14	0.34	0.09	0.08	1.98	1.65	0.33
Mongolia	MN01	1st	5.1	4.4	NA	NA	NA	NA	2.47	1.65	0.82
		2nd	5.0	4.3	NA	NA	NA	NA	2.47	1.65	0.82
Philippines	PH01	1st	4.9	4.1 c	1.79	0.42	0.09	0.03 g	1.94 c	1.89	0.24
		2nd	4.9	4.2 c	1.82	0.43	0.09	0.04 g	1.97 c	1.91	0.25
Vietnam	VN01	1st	4.9	4.1	2.12	0.52	0.11	0.08	2.27	2.01	0.40
		2nd	4.9	4.1	2.13	0.53	0.11	0.08	2.27	2.01	0.40
	VN02	1st	5.0	4.0	NA	NA	NA	NA	2.28	2.04	2.52 g
		2nd	5.0	4.0	NA	NA	NA	NA	2.28	2.04	2.52 g
	VN04	1st	4.6 g	4.2	2.11	0.51	0.11	0.08	2.21	1.96	0.40
		2nd	4.6 g	4.2	2.11	0.52	0.11	0.08	2.21	1.96	0.40
	VN05	1st	5.0	4.0	NA	NA	NA	NA	NA	NA	NA
		2nd	5.0	4.0	NA	NA	NA	NA	NA	NA	NA

The outliers were determined by Cochran and Grubbs tests, and were indicated by "c" and "g" signs, respectively.

4.3.3 Statistical summary for verified data

The statistical summary for verified datasets in No.231s and No.232s is shown in Table 4.4. This year, zero to two laboratories were rejected due to outliers for all measured items, resulting in slight changes to the total averages. However, the data variability (CVs) of almost all items decreased compared to the entire dataset. Nevertheless, these variations are still too large for accurate comparison of the regular monitoring data among the participating countries. The variation may include errors arising from the by same conditions (repetition), different personnel, times, or instruments (within-laboratory), or different laboratories (inter-laboratory). We will explore this variation further in the next section to identify its sources.

Table 4.4 Basic statistics of the verified[*2] dataset

Statistics	$pH(H_2O)$	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
			cmol$_c$ kg^{-1}						
	No. 231s								
Number of Laboratories	5	7	5	5	5	5	7	6	5
Total average	4.6	4.2	0.19	0.11	0.15	0.07	3.71	3.47	0.35
Median	4.6	4.1	0.22	0.07	0.16	0.07	3.72	3.52	0.42
Maximum	4.7	4.3	0.31	0.18	0.17	0.11	5.18	4.75	0.43
Minimum	4.6	4.1	0.04	0.06	0.11	0.02	2.06	1.93	0.13
Standard deviation	0.1	0.1	0.13	0.06	0.03	0.03	0.93	0.92	0.13
CV (%)[*1]	1.3	2.2	68.8	56.6	20.0	49.5	24.9	26.4	37.9
	No. 232s								
Number of Laboratories	7	7	5	5	5	4	5	6	6
Total average	5.0	4.1	2.03	0.43	0.10	0.08	2.24	1.87	0.37
Median	5.0	4.1	2.11	0.42	0.11	0.08	2.27	1.93	0.37
Maximum	5.1	4.3	2.16	0.53	0.11	0.08	2.47	2.04	0.82
Minimum	4.9	4.0	1.81	0.34	0.09	0.07	1.98	1.64	0.04
Standard deviation	0.1	0.1	0.15	0.08	0.01	0.01	0.18	0.18	0.26
CV (%)[*1]	1.3	2.7	7.6	19.5	9.5	6.8	7.9	9.6	68.8

*1: CV, Coefficient of variance (%) = (standard deviation/average)*100

*2: Outliers determined by Cochran-Grubbs tests and obvious calculation mistakes were removed.

4.3.4 Analysis of variance for verified data

“Repeatability precision”, “within-laboratory precision”, and “inter-laboratories precision” were discussed using analysis of variance (ANOVA) to detect the source of data variability (Table 4.5).

1) Repeatability precision

The repeatability precision was sufficiently high for all items, with CVs below 0.7% in $pH(H_2O)$ and pH(KCl), and below 10% in Ex-base cations, Ex-acidity, Ex-Al, and Ex-H. These results suggest that triplicate analyses were carried out under consistent conditions. Overall, participating laboratories were able to analyze the parameters using their own standard procedures and stable instruments effectively.

2) Within-laboratory precision

CVs for almost all parameters in within-laboratory precision were smaller than those in repeatability precision. This suggests that the average of triplicate analyses under repeatability conditions could serve as a representative value for the analysis in a laboratory. We assumed that participating laboratories were able to analyze the parameters using their own standard procedures effectively.

3) Inter-laboratories precision

CVs for inter-laboratories precision were less than 3% in $pH(H_2O)$ and pH(KCl). However, for the remaining parameters, CVs ranged from 7 to 70%. Therefore, in this inter-laboratory comparison, most errors in each parameter were attributed to differences between laboratories. We will discuss the possible factors contributing to the relatively high CVs in inter-laboratories precision in the following section.

4) Calculation of permissible tolerance

The repeatability limit and within-laboratory reproducibility limit may be sufficiently small to serve as reference values for repeated instrumental analyses in respective laboratories. Participating laboratories can detect significant changes in the temporal pH data at each site if the differences exceed 0.1 pH units. Additionally, the reproducibility limit (inter-laboratories reproducibility limit) suggests that participating laboratories can detect significant differences between monitoring sites if the differences are greater than approximately 0.2-0.3 for pH(H_2O) and pH(KCl), 0.01-0.43 $cmol_c\ kg^{-1}$ for Ex-base cations, 2.6 $cmol_c\ kg^{-1}$ for Ex-acidity, 2.6 $cmol_c\ kg^{-1}$ for Ex-Al, and 0.72 $cmol_c\ kg^{-1}$ for Ex-H.

Table 4.5 Analysis of variance for the verified dataset

Statistics	No. 231s								
	pH(H_2O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
Number of Laboratories	5	7	5	5	5	5	7	6	5
Total sum of square	19000	31000	32	10	19	3.9	24000	16000	110
ST/lmd	640	730	1.1	0.35	0.65	0.13	580	430	3.6
Number of Laboratories	5	7	5	5	5	5	7	6	5
Number of Data	30	42	30	30	30	30	42	36	30
Total sum	140	170	5.6	3.2	4.4	2.0	160	120	10
Total average	4.6	4.2	0.19	0.11	0.15	0.07	3.71	3.47	0.35
Sum of square inter-laboratories (S_R)	0.1	0.3	0.40	0.09	0.02	0.03	30.89	25.12	0.41
Sum of square within-laboratory (S_{RW})	0.0	0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sum of square repeatablility (S_r)	0.0	0.0	0.00	0.00	0.00	0.00	0.10	0.10	0.02
Total sum of square (S_T)	0.1	0.3	0.40	0.09	0.02	0.03	30.99	25.22	0.43
Inter-laboratories degree of freedom (ϕ_R)	4	6	4	4	4	4	6	5	4
Within-laboratory degree of freedom (ϕ_{RW})	5	7	5	5	5	5	7	6	5
Repeatability degree of freedom (ϕ_r)	20	28	20	20	20	20	28	24	20
Total degree of freedom (ϕ_T)	29	41	29	29	29	29	41	35	29
Inter-laboratories variance ($V_R = S_R/\phi_R$)	0.0	0.0	0.10	0.02	0.01	0.01	5.15	5.02	0.10
Within-laboratory variance ($V_{RW} = S_{RW}/\phi_{RW}$)	0.0	0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Repeatability variance ($V_r = S_r/\phi_r$)	0.0	0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Laboratory component of variance ($s_b^2 = (V_R - V_{RW})/(2 \times 3)$)	0.0	0.0	0.02	0.00	0.00	0.00	0.86	0.84	0.02
Within-laboratory component of variance ($s_c^2 = (V_{RW} - V_r)/3$)	0.0	0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Repeatability component of variance ($s_r^2 = V_r$)	0.0	0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Inter-laboratories standard deviation ($s_R = SQRT(s_r^2/(2\times3) + s_c^2/2 + s_b^2)$)	0.1	0.1	0.13	0.06	0.03	0.03	0.93	0.92	0.13
Within-laboratory standard deviation ($s_{RW} = SQRT(s_r^2/3 + s_c^2)$)	0.0	0.0	0.00	0.00	0.00	0.00	0.01	0.02	0.00
Repeatability standard deviation ($s_r = SQRT(s_r^2)$)	0.0	0.0	0.01	0.00	0.00	0.01	0.06	0.06	0.03
Inter-laboratories precision CV (%)	1.3	2.2	68.84	56.61	20.00	49.54	24.94	26.40	37.95
Within-laboratory precision CV (%)	0.1	0.2	2.40	1.29	1.14	3.97	0.14	0.44	0.85
Repeatability precision CV (%)	0.3	0.2	3.99	3.83	3.31	10.21	1.58	1.84	9.01
Reproducibility limit ($R = D(2, 0.95)\times s_R$)	0.2	0.3	0.36	0.17	0.08	0.09	2.59	2.56	0.37
Within-laboratory-reproducibility limit ($R_W = D(2, 0.95)\times s_{Rw}$)	0.0	0.0	0.01	0.00	0.00	0.01	0.01	0.04	0.01
Repeatability limit ($r = D(3, 0.95)\times s_r$)	0.0	0.0	0.02	0.01	0.02	0.02	0.19	0.21	0.10

Table 4.5 Analysis of variance for the verified dataset (continued)

Statistics	No. 232s								
	$pH(H_2O)$	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
Number of Laboratories	7	7	5	5	5	4	5	6	6
Total sum of square	44000	30000	3700	170	9.6	3.4	4500	4500	180
ST/lmd	1000	720	120	5.6	0.32	0.14	150	130	5.1
Number of Laboratories	7	7	5	5	5	4	5	6	6
Number of Data	42	42	30	30	30	24	30	36	36
Total sum	210	170	61	13	3.1	1.8	67	67	13
Total average	5.0	4.1	2.03	0.43	0.10	0.08	2.24	1.87	0.37
Sum of square inter-laboratories (S_R)	0.2	0.5	0.57	0.17	0.00	0.00	0.74	0.97	2.00
Sum of square within-laboratory (S_{RW})	0.0	0.0	0.01	0.00	0.00	0.00	0.00	0.00	0.00
Sum of square repeatablility (S_r)	0.0	0.0	0.03	0.00	0.00	0.00	0.02	0.01	0.02
Total sum of square (S_T)	0.2	0.5	0.61	0.17	0.00	0.00	0.76	0.98	2.02
Inter-laboratories degree of freedom (ϕ_R)	6	6	4	4	4	3	4	5	5
Within-laboratory degree of freedom (ϕ_{RW})	7	7	5	5	5	4	5	6	6
Repeatability degree of freedom (ϕ_r)	28	28	20	20	20	16	20	24	24
Total degree of freedom (ϕ_T)	41	41	29	29	29	23	29	35	35
Inter-laboratories variance ($V_R = S_R/\phi_R$)	0.0	0.1	0.14	0.04	0.00	0.00	0.19	0.19	0.40
Within-laboratory variance ($V_{RW} = S_{RW}/\phi_{RW}$)	0.0	0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Repeatability variance ($V_r = S_r/\phi_r$)	0.0	0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Laboratory component of variance ($s_b^2 = (V_R\text{-}V_{RW})/(2\times3)$)	0.0	0.0	0.02	0.01	0.00	0.00	0.03	0.03	0.07
Within-laboratory component of variance ($s_c^2 = (V_{RW}\text{-}V_r)/3$)	0.0	0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Repeatability component of variance ($s_r^2 = V_r$)	0.0	0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Inter-laboratories standard deviation ($s_R = SQRT(s_r^2/(2\times3) + s_c^2/2 + s_b^2)$)	0.1	0.1	0.15	0.08	0.01	0.01	0.18	0.18	0.26
Within-laboratory standard deviation ($s_{RW} = SQRT(s_r^2/3 + s_c^2)$)	0.0	0.0	0.02	0.00	0.00	0.00	0.00	0.01	0.01
Repeatability standard deviation ($s_r = SQRT(s_r^2)$)	0.0	0.0	0.04	0.01	0.01	0.00	0.03	0.02	0.03
Inter-laboratories precision CV (%)	1.3	2.7	7.61	19.53	9.47	6.77	7.85	9.63	68.79
Within-laboratory precision CV (%)	0.3	0.3	1.07	1.07	1.11	4.56	0.11	0.44	2.25
Repeatability precision CV (%)	0.7	0.3	1.97	2.26	5.34	4.84	1.24	1.27	7.90
Reproducibility limit ($R = D(2, 0.95)\times s_R$)	0.2	0.3	0.43	0.24	0.03	0.01	0.49	0.50	0.72
Within-laboratory-reproducibility limit ($R_W = D(2, 0.95)\times s_{Rw}$)	0.0	0.0	0.06	0.01	0.00	0.01	0.01	0.02	0.02
Repeatability limit ($r = D(3, 0.95)\times s_r$)	0.1	0.0	0.13	0.03	0.02	0.01	0.09	0.08	0.10

4.3.5 Inter-laboratory variations in each parameter

To assess precision in each laboratory and property, scatter plots between No.231s and No.232s are shown (Figure 4.2). The plots have been adjusted to remove extreme outliers for better readability.

1) pH

A linear and positive correlation was observed between No.231s and No.232s for pH(KCl), indicating systematic errors in inter-laboratory variation. These errors might be caused by conditions such as the purity of water, standard solution, or glass electrode. Additionally, factors such as the stabilization time for the value could contribute to variation, as carbon dioxide pressure, leakage of KCl solution from the electrode, and settling of clay particles in the sample tube can alter the ion balance in soil suspension. For $pH(H_2O)$, the limited number of laboratories may have influenced the unclear relationships.

2) Base cations

Due to the limited number of participating laboratories this year, no correlations were found for exchangeable base cations. Laboratories that were rejected by outlier tests should pay attention to factors such as the purity of water, standard solutions, and so on. In the analysis of base cations, higher concentrations or a higher pH of the extraction solution may result in increase of the base cation concentrations. It is important to prepare appropriate standard solutions covering a range of concentrations from low to high, which completely encompass the concentrations of unknown samples, to reduce errors. Using extraction solution for dilution of standards can also minimize the matrix effect.

3) Acidity

Weak positive and linear correlations were observed for Ex-acidity, Ex-Al, and Ex-H. To reduce errors, analysts should pay attention to titration manipulation, which can be easily affected by factors such as volumetric solution or end-point detection. In the definition, Ex-acidity is sum of Ex-Al and Ex-H. It is strongly recommended to check whether each parameter falls within the expected range of this relationship before submitting the results.

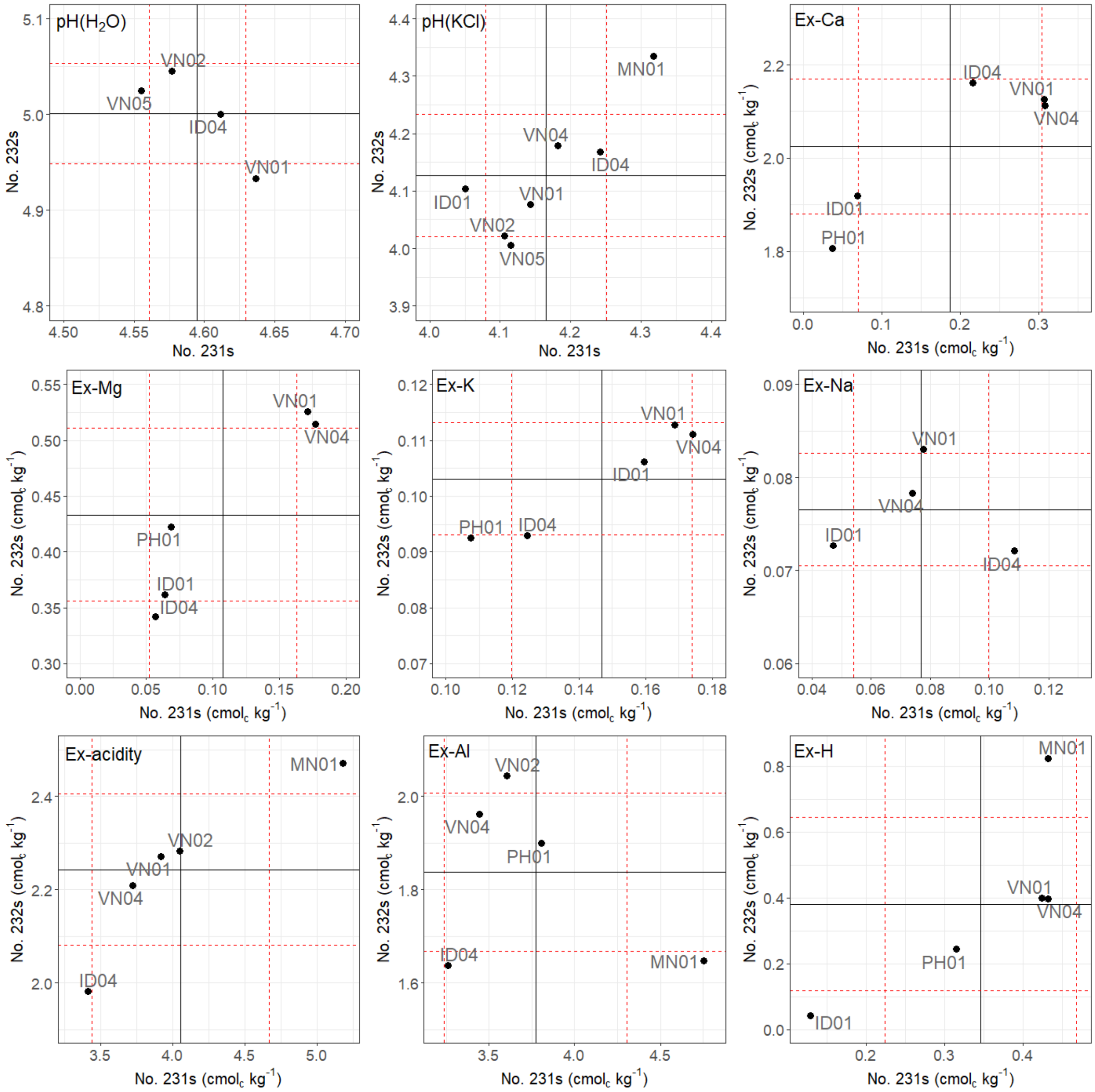


Figure 4.2 Scatter plots of each soil chemical property between No.231s and No.232s
Solid and dotted lines indicate mean and mean ± S.D. of verified datasets, respectively.
The outliers are excluded from the plots.

4.3.6 Comparison with information on Laboratories

1) Number of analysts and their experience

Table 4.6 displays the number of analysts and their years of experience. Specialization in analysis, where analysts vary depending on the type of analysis, is becoming common. No discernible relationship was found between the number of analysts, their years of experience, and the occurrence of outliers.

Table 4.6 Number of analyst and years of experience

Lab.	Ex-base cations			Ex-acidity			Analyst
	Number of analyst	Years of experience		Number of analyst	Years of experience		
		Chemical	Soil		Chemical	Soil	
ID04	1	6	0	1	6	0	s
ID04	1	2	2	1	5	5	d
MN01	-	-	-	1	19	12	-
PH01	1	4	3	1	4	2	d
VN01	1	10	10	1	7	7	d
VN02	-	-	-	1	19	15	-
VN04	1	17	16	1	19	18	d
VN05	-	-	-	-	-	-	-

Note: -, Not analyzed; n, no information; s, Same analysts; d, Different analysts

2) Analytical instruments and condition of instruments

Table 4.7 presents the analytical instruments used for measurement, extraction procedures for Ex-base cations, and size of burettes used for the titration method in Ex-acidity. All Ex-base cations were analyzed using AAS. The instruments have been in use for periods ranging from 3 to 17 years. Two laboratories employed the Buchner funnel procedure, two used the centrifuge procedure, and one used the percolation tube procedure for the extraction of Ex-base cations. No significant differences were observed among the various procedures. Ranging the size of burettes used for the titration of Ex-acidity, capacities ranged from 10 to 50 mL, with minimum graduations varying from 0.01 to 0.1.

3) Date of analysis

The dates of analysis conducted in the respective laboratories and the numbers of days taken for the analysis are presented in Table 4.8. There was no significant correlation between the date of analysis and the data. The duration of analysis ranged from 1 to 25 days, and the interval between the first and second analyses of repeat analyses varied from 0 (on the same day) to 24 days. It is recommended that repeat analyses be conducted with an interval of several days (three days or more) to accurately estimate within-laboratory reproducibility. This recommendation is based on discussions held at SAC 3 (the Third Session of the Scientific Advisory Committee on EANET).

Table 4.7 Analytical instruments and their conditions for Ex- cations

Lab.	Sample	Procedures for extraction of Ex-base cations	Ex-Ca		Ex-Mg		Interference depressant	Ex-K		Ex-Na		Interference depressant	Ex-Acidity, Al and H		
													method	Size of burette (mL)	
			Instrument	Years*1	Instrument	Years	for Ca and Mg	Instrument	Years	Instrument	Years	for K and Na		Capacity	Minimum graduate
ID01	231s	Centrifuge	AAS	4	AAS	4	Sr	AAS	9	AAS	4	Sr	Titration	50	0.1
	232s		AAS	4	AAS	4	Sr	AAS	9	AAS	4	Sr		50	0.1
ID04	231s	Percolation tube	AAS	9	AAS	9	La	AAS	9	AAS	9	La	Titration	25	0.02
	232s		AAS	9	AAS	9	La	AAS	9	AAS	9	La		25	0.02
MN01	231s						-						Titration	25	0.1
	232s													25	0.1
PH01	231s	Centrifuge	AAS	3	AAS	3	La	AAS	3	AAS	3	na	Titration	25	0.01
	232s		AAS	3	AAS	3	La	AAS	3	AAS	3	La		25	0.01
VN01	231s	Buchner funnel	AAS	16	AAS	16	+	AAS	16	AAS	16	+	Titration	10	0.05
	232s		AAS	16	AAS	16	+	AAS	16	AAS	16	+		10	0.05
VN02	231s						-						Titration	10	0.05
	232s													10	0.05
VN04	231s	Buchner funnel	AAS	17	AAS	17	na	AAS	17	AAS	16	na	Titration	10	0.01
	232s		AAS	17	AAS	17	na	AAS	17	AAS	16	na		10	0.01
VN05	231s							-							
	232s														

*1, years in use of instrument; -, not measured; AAS, Atomic Absorption Spectrometry; ICP-AES, Inductively Coupled Plasma-Atomic Emission Spectrometry; na, not added; +, not reported.

Table 4.8 Date of analysis

Lab.	Repeat	pH				Ex-Ca and Mg				Ex-K and Na				Ex-acidity, Al and H			
		Start Date	Finish Date	AD	ID	Start Date	Finish Date	AD	ID	Start Date	Finish Date	AD	ID	Start Date	Finish Date	AD	ID
				Days				Days				Days				Days	
ID01	1st	2024/1/4	2024/1/4	1	21	2024/2/1	2024/2/5	5	18	2024/2/1	2024/2/5	5	18	2024/1/8	2024/1/9	2	21
	2nd	2024/1/25	2024/1/25	1		2024/2/20	2024/2/23	4		2024/2/20	2024/2/23	4		2024/1/29	2024/1/30	2	
ID04	1st	2023/11/9	2023/11/9	1	7	2023/11/9	2023/11/9	1	7	2023/11/9	2023/11/9	1	7	2023/11/9	2023/11/9	1	7
	2nd	2023/11/16	2023/11/16	1		2023/11/16	2023/11/16	1		2023/11/16	2023/11/16	1		2023/11/16	2023/11/16	1	
MN01	1st	2024/2/5	2024/2/5	1	3	NA				NA				2024/2/5	2024/2/5	1	3
	2nd	2024/2/8	2024/2/8	1										2024/2/8	2024/2/8	1	
PH01	1st	2024/1/16	2024/1/16	1	15	2024/2/6	2024/2/13	8	17	2024/2/6	2024/2/13	8	17	2024/2/1	2024/2/13	13	24
	2nd	2024/1/31	2024/1/31	1		2024/2/14	2024/3/1	17		2024/2/14	2024/3/1	17		2024/2/13	2024/3/8	25	
VN01	1st	2023/12/6	2023/12/6	1	2	2023/12/5	2023/12/6	2	2	2023/12/5	2023/12/6	2	2	2023/12/6	2023/12/7	2	1
	2nd	2023/12/8	2023/12/8	1		2023/12/7	2023/12/8	2		2023/12/7	2023/12/8	2		2023/12/7	2023/12/8	2	
VN02	1st	2023/12/25	2023/12/25	1	0	NA				NA				2023/12/26	2023/12/27	2	0
	2nd	2023/12/25	2023/12/25	1										2023/12/26	2023/12/27	2	
VN04	1st	2023/12/4	2023/12/4	1	2	2023/12/4	2023/12/4	1	2	2023/12/4	2023/12/4	1	2	2023/12/15	2023/12/15	1	0
	2nd	2023/12/6	2023/12/6	1		2023/12/6	2023/12/6	1		2023/12/6	2023/12/6	1		2023/12/15	2023/12/15	1	
VN05	1st	2024/1/15	2024/1/16	2	1	NA				NA				NA			
	2nd	2024/1/16	2024/1/17	2													

AD, days for analysis; ID; interval between the repeat analyses; +, not reported; NA, not analyzed.

4.3.7 Detection limit and quantification limit

Since the 21st project, detection limits and quantification limits for Ex-base cations have been required to be reported. All laboratories that analyzed Ex-base cations reported these values (Table 4.9). The detection limits for Ex-Ca, Ex-Mg, Ex-K, and Ex-Na ranged from 0.03 to 0.08, 0.01 to 0.076, 0.015 to 0.06, and 0.01 to 0.05 mg/L, respectively. Similarly, the quantification limits for Ex-Ca, Ex-Mg, Ex-K, and Ex-Na ranged from 0.05 to 0.3, 0.02 to 0.254, 0.05 to 0.2, and 0.03 to 0.2 mg/L, respectively. Figure 4.3 compares these limit values with the concentrations of soil extracts. For almost all analyzed items and laboratories, except for Na in ID04, the concentrations of soil extracts exceeded the quantification limit by at least one digit, suggesting that the analyses of Ex-base cations were conducted with a sufficient margin of capacity.

Table 4.9 Detection limit and quantification limit of each laboratory

Lab.	Ex-Ca			Ex-Mg			Ex-K			Ex-Na		
	DL	QL	unit	DL	QL	unit	DL	QL	unit	DL	QL	unit
ID01	0.08	0.3	mg/L	0.03	0.09	mg/L	0.06	0.2	mg/L	0.04	0.1	mg/L
ID04	0.03	0.09	mg/L	0.01	0.02	mg/L	0.02	0.08	mg/L	0.05	0.2	mg/L
MN01	-	-	-	-	-	-	-	-	-	-	-	-
PH01	0.05	0.05	mg/L	0.05	0.05	mg/L	0.05	0.05	mg/L	0.05	0.05	mg/L
VN01	0.05	0.15	mg/L	0.02	0.06	mg/L	0.03	0.09	mg/L	0.01	0.03	mg/L
VN02	-	-	-	-	-	-	-	-	-	-	-	-
VN04	0.073	0.242	mg/L	0.076	0.254	mg/L	0.015	0.05	mg/L	0.015	0.05	mg/L
VN05	-	-	-	-	-	-	-	-	-	-	-	-

DL, detection limit; QL, quantification limit; -, not reported or not analyzed.

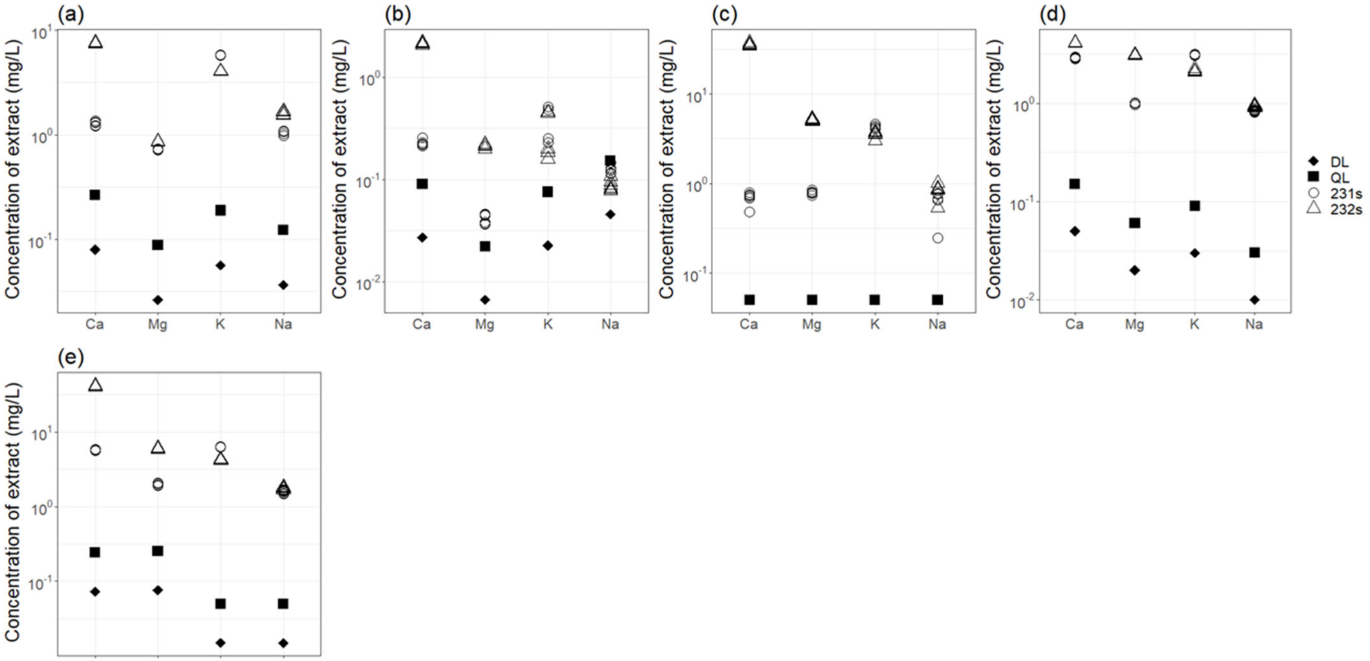


Figure 4.3 Detection limit, quantification limit and concentrations of soil extracts
(a) ID01, (b) ID04, (c) PH01, (d) VN01, (e) VN04
DL, detection limit; QL, quantification limit

4.4 Needs for improvement of soil analyses

Figure 4.4 illustrates the change in outlier ratios across all items and laboratories from 2002 to 2023. Despite a decrease since the initial experiment in 2002, the ratio remains relatively high (10-25% from 2003 to 2023). However, both outlier ratios for samples 231s and 232s (i.e., 2023_1 and 2023_2, respectively) were lower than the average outlier ratio from 2003 to 2022. Outliers can disrupt the evaluation and understanding of actual monitoring data. Therefore, reducing the occurrence of outliers is a crucial task for future inter-laboratory comparison projects on soil. It is essential to review appropriate standard solutions, extraction methods, dilution rates, and calculations to mitigate the presence of extremely divergent values classified as outliers.

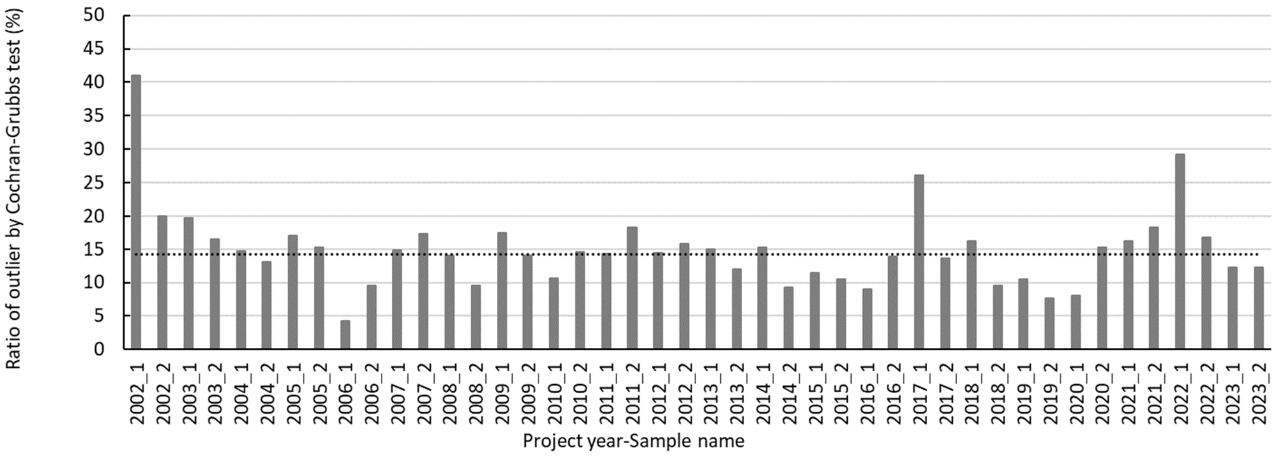


Figure 4.4 Change in outlier ratios in all items and laboratories from 2002 to 2022.
Outlier ratio = {(*N* of entire dataset) – (*N* of verified dataset)} / (*N* of entire dataset).
The suffixes '_1' and '_2' denote the two types of the samples analyzed each year (e.g., 231s and 232s).
Outlier ratios from 2002 to 2022 were obtained from the *Report of Inter-Laboratory Comparison Project 2000-2022* (https://monitoring.eanet.asia/document/public/index).
The dotted line indicates the average outlier ratio from 2003 to 2022.

4.5 Recommendations for improvement

Priority should be given to reducing outliers in Ex-base and acid cations. Additionally, efforts should be made to enhance precision for samples with low concentrations. This entails examining the conditions of standard solutions, extraction methods, dilution rates, calculations, and equipment operation. Analysts should strive to improve procedural standards within each laboratory. It is also important to meticulously review not only analytical procedures but also reporting procedures.

References

EANET (2000). *Technical Documents for Soil and Vegetation Monitoring in East Asia*: Acid Deposition and Oxidant Research Center, Niigata, Japan.

Appendix Table 4.1 Results submitted by the laboratories (sample No. 231s)

Lab	pH(H_2O)			pH(KCl)			Ex-Ca (cmol$_c$ kg^{-1})			Ex-Mg (cmol$_c$ kg^{-1})			Ex-K (cmol$_c$ kg^{-1})			Ex-Na (cmol$_c$ kg^{-1})			Ex-Acidity (cmol$_c$ kg^{-1})			Ex-Al (cmol$_c$ kg^{-1})			Ex-H (cmol$_c$ kg^{-1})		
	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat
ID01	4.3	4.3	4.3	4.1	4.0	4.0	0.07	0.07	0.07	0.06	0.06	0.06	0.16	0.16	0.16	0.05	0.05	0.05	2.06	2.06	2.06	1.93	1.93	1.93	0.13	0.13	0.13
	(0.0)	(0.0)	4.3	(0.0)	(0.0)	4.1	(0.00)	(0.00)	0.07	(0.00)	(0.00)	0.06	(0.00)	(0.00)	0.16	(0.00)	(0.00)	0.05	(0.00)	(0.00)	2.06	(0.00)	(0.00)	1.93	(0.00)	(0.00)	0.13
			4.3			4.1			0.07			0.06			0.16			0.05			2.06			1.93			0.13
		4.3	4.3		4.1	4.1		0.07	0.06		0.06	0.06		0.16	0.16		0.05	0.05		2.06	2.06		1.93	1.93		0.13	0.13
		(0.0)	4.3		(0.0)	4.1		(0.00)	0.07		(0.00)	0.06		(0.00)	0.16		(0.00)	0.05		(0.00)	2.06		(0.00)	1.93		(0.00)	0.13
			4.3			4.1			0.07			0.06			0.16			0.05			2.06			1.93			0.13
ID04	4.6	4.6	4.6	4.2	4.2	4.3	0.22	0.22	0.20	0.06	0.06	0.06	0.12	0.12	0.13	0.11	0.11	0.10	3.41	3.40	3.43	3.26	3.27	3.29	0.15	0.13	0.14
	(0.0)	(0.0)	4.6	(0.0)	(0.0)	4.2	(0.01)	(0.02)	0.24	(0.00)	(0.00)	0.06	(0.01)	(0.01)	0.12	(0.01)	(0.00)	0.10	(0.03)	(0.02)	3.39	(0.04)	(0.02)	3.25	(0.03)	(0.02)	0.14
			4.6			4.2			0.22			0.06			0.12			0.11			3.39			3.29			0.10
		4.6	4.6		4.2	4.2		0.21	0.22		0.06	0.06		0.13	0.12		0.11	0.10		3.42	3.38		3.25	3.20		0.17	0.18
		(0.0)	4.6		(0.0)	4.2		(0.01)	0.21		(0.00)	0.06		(0.01)	0.12		(0.01)	0.13		(0.03)	3.45		(0.04)	3.29		(0.01)	0.16
			4.6			4.3			0.21			0.06			0.13			0.11			3.43			3.25			0.18
MN01	4.9	4.9	4.9	4.3	4.3	4.3	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	5.18	5.18	5.18	4.75	4.75	4.75	0.43	0.43	0.43
	(0.1)	(0.1)	4.8	(0.0)	(0.0)	4.3			NA			NA			NA			NA	(0.00)	(0.00)	5.18	(0.00)	(0.00)	4.75	(0.00)	(0.00)	0.43
			4.9			4.3			NA			NA			NA			NA			5.18			4.75			0.43
		4.9	4.9		4.3	4.3		NA	NA		NA	NA		NA	NA		NA	NA		5.18	5.18		4.75	4.75		0.43	0.43
		(0.1)	4.9		(0.0)	4.3			NA			NA			NA			NA		(0.00)	5.18		(0.00)	4.75		(0.00)	0.43
			5.0			4.3			NA			NA			NA			NA			5.18			4.75			0.43
PH01	4.6	4.6	4.6	4.2	4.1	4.2	0.04	0.04	0.04	0.07	0.07	0.07	0.11	0.11	0.10	0.02	0.02	0.02	3.65	3.66	3.88	3.81	3.83	3.91	0.32	0.32	0.25
	(0.0)	(0.0)	4.6	(0.1)	(0.0)	4.1	(0.01)	(0.00)	0.04	(0.00)	(0.00)	0.07	(0.01)	(0.00)	0.11	(0.01)	(0.00)	0.02	(0.13)	(0.20)	3.54	(0.12)	(0.07)	3.79	(0.06)	(0.08)	0.40
			4.5			4.1			0.04			0.07			0.11			0.02			3.54			3.79			0.30
		4.5	4.6		4.2	4.2		0.03	0.04		0.07	0.06		0.11	0.10		0.02	0.03		3.65	3.72		3.78	3.58		0.31	0.26
		(0.0)	4.5		(0.0)	4.2		(0.01)	0.04		(0.00)	0.07		(0.01)	0.12		(0.01)	0.01		(0.06)	3.61		(0.18)	3.88		(0.05)	0.35
			4.5			4.2			0.03			0.07			0.11			0.03			3.61			3.90			0.31
VN01	4.6	4.6	4.6	4.1	4.2	4.2	0.31	0.30	0.31	0.17	0.17	0.17	0.17	0.17	0.17	0.08	0.08	0.08	3.92	3.92	3.90	3.51	3.46	3.43	0.42	0.42	0.42
	(0.0)	(0.0)	4.7	(0.0)	(0.0)	4.2	(0.00)	(0.00)	0.31	(0.00)	(0.00)	0.18	(0.00)	(0.00)	0.17	(0.00)	(0.00)	0.08	(0.02)	(0.02)	3.94	(0.07)	(0.05)	3.52	(0.03)	(0.04)	0.47
			4.7			4.2			0.30			0.17			0.17			0.08			3.92			3.43			0.38
		4.6	4.6		4.1	4.1		0.31	0.31		0.17	0.17		0.17	0.17		0.08	0.08		3.91	3.88		3.56	3.52		0.42	0.42
		(0.0)	4.6		(0.0)	4.1		(0.00)	0.31		(0.00)	0.17		(0.00)	0.17		(0.00)	0.07		(0.03)	3.94		(0.04)	3.56		(0.00)	0.42
			4.7			4.1			0.31			0.17			0.17			0.08			3.92			3.60			0.42
VN02	4.6	4.6	4.6	4.1	4.1	4.1	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	4.05	4.05	4.01	3.60	3.60	3.53	4.49	4.49	4.49
	(0.0)	(0.0)	4.6	(0.0)	(0.0)	4.1			NA			NA			NA			NA	(0.03)	(0.03)	4.07	(0.06)	(0.06)	3.64	(0.00)	(0.00)	4.49
			4.6			4.1			NA			NA			NA			NA			4.07			3.64			4.49
		4.6	4.6		4.1	4.1		NA	NA		NA	NA		NA	NA		NA	NA		4.05	4.01		3.60	3.53		4.49	4.49
		(0.0)	4.6		(0.0)	4.1			NA			NA			NA			NA		(0.03)	4.07		(0.06)	3.64		(0.00)	4.49
			4.6			4.1			NA			NA			NA			NA			4.07			3.64			4.49
VN04	4.7	4.7	4.7	4.2	4.2	4.2	0.31	0.31	0.30	0.18	0.18	0.17	0.17	0.17	0.17	0.07	0.07	0.07	3.72	3.72	3.73	3.44	3.44	3.46	0.43	0.43	0.43
	(0.0)	(0.0)	4.7	(0.0)	(0.0)	4.2	(0.00)	(0.01)	0.30	(0.01)	(0.01)	0.17	(0.00)	(0.00)	0.18	(0.00)	(0.00)	0.08	(0.01)	(0.01)	3.73	(0.02)	(0.02)	3.46	(0.00)	(0.00)	0.43
			4.7			4.2			0.31			0.19			0.18			0.07			3.72			3.41			0.43
		4.7	4.7		4.2	4.2		0.31	0.31		0.18	0.19		0.17	0.18		0.08	0.07		3.72	3.73		3.44	3.46		0.43	0.43
		(0.0)	4.7		(0.0)	4.2		(0.00)	0.31		(0.01)	0.17		(0.00)	0.17		(0.00)	0.08		(0.01)	3.73		(0.02)	3.46		(0.00)	0.43
			4.7			4.2			0.31			0.17			0.17			0.08			3.72			3.41			0.43
VN05	4.6	4.7	4.7	4.1	4.2	4.2	0.31	0.31	0.31	0.17	0.17	0.17	0.17	0.17	0.17	0.08	0.08	0.08	3.72	3.72	3.73	3.43	3.43	3.46	0.43	0.43	0.43
	(0.1)	(0.1)	4.7	(0.0)	(0.0)	4.2	(0.00)	(0.00)	0.31	(0.00)	(0.00)	0.17	(0.00)	(0.00)	0.17	(0.00)	(0.00)	0.08	(0.01)	(0.01)	3.72	(0.03)	(0.03)	3.41	(0.00)	(0.00)	0.43
			4.6			4.1			NA			NA			NA			NA			NA			NA			NA
		4.6	4.6		4.1	4.1		NA	NA		NA	NA		NA	NA		NA	NA		NA	NA		NA	NA		NA	NA
		(0.0)	4.6		(0.0)	4.1			NA			NA			NA			NA			NA			NA			NA
			4.6			4.1			NA			NA			NA			NA			NA			NA			NA

Appendix Table 4.2 Results submitted by the laboratories (sample No. 232s)

Lab	pH(H_2O)			pH(KCl)			Ex-Ca (cmol$_c$ kg^{-1})			Ex-Mg (cmol$_c$ kg^{-1})			Ex-K (cmol$_c$ kg^{-1})			Ex-Na (cmol$_c$ kg^{-1})			Ex-Acidity (cmol$_c$ kg^{-1})			Ex-Al (cmol$_c$ kg^{-1})			Ex-H (cmol$_c$ kg^{-1})		
	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat
ID01	5.0	5.0	5.0	4.1	4.1	4.1	1.92	1.94	1.96	0.36	0.36	0.36	0.11	0.11	0.11	0.07	0.07	0.07	0.74	0.74	0.74	0.70	0.70	0.70	0.04	0.04	0.04
	(0.0)	(0.0)	5.0	(0.0)	(0.0)	4.1	(0.02)	(0.02)	1.93	(0.00)	(0.00)	0.36	(0.00)	(0.00)	0.11	(0.00)	(0.00)	0.07	(0.00)	(0.00)	0.74	(0.00)	(0.00)	0.70	(0.00)	(0.00)	0.04
			5.0			4.1			1.92			0.36			0.11			0.07			0.74			0.70			0.04
		5.0	5.0		4.1	4.1		1.90	1.89		0.36	0.36		0.11	0.11		0.07	0.08		0.74	0.74		0.70	0.70		0.04	0.04
		(0.0)	5.0		(0.0)	4.1		(0.02)	1.93		(0.00)	0.36		(0.00)	0.11		(0.00)	0.07		(0.00)	0.74		(0.00)	0.70		(0.00)	0.04
			5.0			4.1			1.90			0.36			0.11			0.07			0.74			0.70			0.04
ID04	5.0	5.0	5.0	4.2	4.2	4.2	2.16	2.18	2.17	0.34	0.34	0.33	0.09	0.09	0.09	0.07	0.07	0.07	1.98	1.98	1.98	1.64	1.63	1.65	0.34	0.36	0.32
	(0.0)	(0.0)	5.0	(0.0)	(0.0)	4.2	(0.04)	(0.02)	2.17	(0.01)	(0.01)	0.35	(0.01)	(0.00)	0.10	(0.01)	(0.00)	0.07	(0.04)	(0.05)	1.94	(0.03)	(0.05)	1.65	(0.03)	(0.03)	0.36
			5.0			4.2			2.21			0.34			0.09			0.07			2.04			1.57			0.38
		5.0	5.0		4.2	4.2		2.14	2.17		0.34	0.33		0.09	0.08		0.08	0.07		1.98	1.99		1.65	1.63		0.33	0.36
		(0.0)	5.0		(0.0)	4.2		(0.04)	2.15		(0.01)	0.35		(0.01)	0.10		(0.01)	0.09		(0.02)	1.99		(0.01)	1.65		(0.03)	0.34
			5.0			4.2			2.09			0.35			0.09			0.07			1.95			1.65			0.30
MN01	5.1	5.1	5.1	4.3	4.4	4.4	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	2.47	2.47	2.47	1.65	1.65	1.65	0.82	0.82	0.82
	(0.0)	(0.0)	5.1	(0.0)	(0.0)	4.4			NA			NA			NA			NA	(0.00)	(0.00)	2.47	(0.00)	(0.00)	1.65	(0.00)	(0.00)	0.82
			5.0			4.3			NA			NA			NA			NA			2.47			1.65			0.82
		5.0	5.1		4.3	4.3		NA	NA		NA	NA		NA	NA		NA	NA		2.47	2.47		1.65	1.65		0.82	0.82
		(0.1)	5.0		(0.0)	4.3			NA			NA			NA			NA		(0.00)	2.47		(0.00)	1.65		(0.00)	0.82
			5.0			4.3			NA			NA			NA			NA			2.47			1.65			0.82
PH01	4.9	4.9	4.9	4.1	4.1	4.1	1.81	1.79	1.82	0.42	0.42	0.41	0.09	0.09	0.10	0.03	0.03	0.03	1.96	1.94	1.94	1.90	1.89	1.88	0.24	0.24	0.28
	(0.0)	(0.0)	4.9	(0.1)	(0.0)	4.1	(0.06)	(0.04)	1.75	(0.02)	(0.01)	0.43	(0.01)	(0.01)	0.10	(0.01)	(0.01)	0.03	(0.04)	(0.02)	1.97	(0.03)	(0.02)	1.88	(0.04)	(0.04)	0.22
			4.9			4.0			1.79			0.42			0.08			0.02			1.93			1.91			0.20
		4.9	4.9		4.2	4.2		1.82	1.92		0.43	0.41		0.09	0.09		0.04	0.04		1.97	2.04		1.91	1.96		0.25	0.27
		(0.0)	4.8		(0.0)	4.2		(0.08)	1.76		(0.02)	0.44		(0.00)	0.09		(0.00)	0.04		(0.06)	1.92		(0.04)	1.90		(0.04)	0.20
			4.9			4.2			1.80			0.44			0.09			0.03			1.95			1.87			0.28
VN01	4.9	4.9	5.0	4.1	4.1	4.1	2.13	2.12	2.12	0.53	0.52	0.52	0.11	0.11	0.11	0.08	0.08	0.08	2.27	2.27	2.23	2.01	2.01	1.98	0.40	0.40	0.37
	(0.1)	(0.1)	4.9	(0.0)	(0.0)	4.1	(0.02)	(0.02)	2.14	(0.01)	(0.01)	0.53	(0.00)	(0.00)	0.11	(0.00)	(0.00)	0.09	(0.03)	(0.04)	2.27	(0.02)	(0.02)	2.02	(0.04)	(0.05)	0.45
			4.9			4.1			2.10			0.52			0.12			0.08			2.31			2.02			0.37
		4.9	5.0		4.1	4.1		2.13	2.14		0.53	0.53		0.11	0.11		0.08	0.08		2.27	2.27		2.01	1.98		0.40	0.37
		(0.1)	4.9		(0.0)	4.1		(0.02)	2.11		(0.01)	0.53		(0.00)	0.11		(0.00)	0.08		(0.03)	2.31		(0.02)	2.02		(0.05)	0.45
			4.9			4.1			2.13			0.52			0.11			0.08			2.25			2.02			0.37
VN02	5.0	5.0	5.1	4.0	4.0	4.0	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	2.28	2.28	2.25	2.04	2.04	2.04	2.52	2.52	2.45
	(0.0)	(0.0)	5.0	(0.0)	(0.0)	4.0			NA			NA			NA			NA	(0.03)	(0.03)	2.30	(0.00)	(0.00)	2.04	(0.05)	(0.06)	2.56
			5.0			4.0			NA			NA			NA			NA			2.30			2.04			2.56
		5.0	5.0		4.0	4.0		NA	NA		NA	NA		NA	NA		NA	NA		2.28	2.25		2.04	2.04		2.52	2.45
		(0.0)	5.1		(0.0)	4.0			NA			NA			NA			NA		(0.03)	2.30		(0.00)	2.04		(0.06)	2.56
			5.1			4.0			NA			NA			NA			NA			2.30			2.04			2.56
VN04	4.6	4.6	4.6	4.2	4.2	4.2	2.11	2.11	2.12	0.51	0.51	0.50	0.11	0.11	0.11	0.08	0.08	0.08	2.21	2.21	2.21	1.96	1.96	1.98	0.40	0.40	0.39
	(0.0)	(0.0)	4.7	(0.0)	(0.0)	4.2	(0.04)	(0.05)	2.06	(0.01)	(0.01)	0.52	(0.00)	(0.00)	0.11	(0.00)	(0.00)	0.08	(0.01)	(0.01)	2.21	(0.02)	(0.02)	1.98	(0.01)	(0.01)	0.39
			4.6			4.2			2.16			0.52			0.11			0.08			2.20			1.93			0.41
		4.6	4.6		4.2	4.2		2.11	2.12		0.52	0.52		0.11	0.11		0.08	0.08		2.21	2.21		1.96	1.98		0.40	0.39
		(0.0)	4.6		(0.0)	4.2		(0.05)	2.06		(0.01)	0.51		(0.00)	0.11		(0.00)	0.08		(0.01)	2.21		(0.02)	1.98		(0.01)	0.39
			4.6			4.2			2.16			0.52			0.11			0.08			2.20			1.93			0.41
VN05	4.9	4.8	4.6	4.1	4.1	4.2	2.11	2.11	2.06	0.51	0.51	0.51	0.11	0.11	0.11	0.08	0.08	0.08	2.21	2.21	2.21	1.96	1.96	1.98	0.40	0.40	0.39
	(0.2)	(0.2)	4.6	(0.1)	(0.1)	4.2	(0.07)	(0.07)	2.16	(0.01)	(0.01)	0.52	(0.00)	(0.00)	0.11	(0.00)	(0.00)	0.08	(0.01)	(0.01)	2.20	(0.03)	(0.03)	1.93	(0.01)	(0.01)	0.41
			5.0			4.0			NA			NA			NA			NA			NA			NA			NA
		5.0	5.0		4.0	4.0		NA	NA		NA	NA		NA	NA		NA	NA		NA	NA		NA	NA		NA	NA
		(0.0)	5.0		(0.0)	4.0			NA			NA			NA			NA			NA			NA			NA
			5.0			4.0			NA			NA			NA			NA			NA			NA			NA

5. 24th INTER-LABORATORY COMPARISON PROJECT ON INLAND AQUATIC ENVIRONMENT

5.1 Introduction

In the Inter-laboratory Comparison Project on inland aquatic environment, an artificial inland water sample containing known concentrations of major ions was prepared and sent to the EANET participating countries by the Network Center (NC). The measured results of pH, EC, alkalinity and concentrations of SO_4^{2-}, NO_3^-, Cl^-, Na^+, K^+, Ca^{2+}, Mg^{2+} and NH_4^+ in the participating laboratories were compared with the prepared values and the results were statistically analyzed.

5.2 Procedures

5.2.1 Participating Laboratories

In the 24th Project, the NC shipped an artificial inland water sample to 17 laboratories involved in the EANET activities on October 17, 2023, and most of them submitted their analytical data to the NC by February 28 2024. Participating laboratories and their identification codes are listed in Table 1.1.

5.2.2 Description of Sample

A description of the sample is given in Table 5.1.

Table 5.1 Description of the artificial inland water sample

Name	Amount of the sample	Container	Number of samples	Note
Artificial inland water sample	Approximately 1 L	Poly-ethylene bottle 1 L	One bottle	To analyze directly

The analytical parameters are shown in Table 5.2.

Table 5.2 Analytical parameters

Analytical Parameter	Reporting Units	
pH	pH units	–
EC	milli siemens per meter	$mS\ m^{-1}$
Alkalinity	milli equivalent per liter	$meq\ L^{-1}$
SO_4^{2-}	milli gram per liter	$mg\ L^{-1}$
NO_3^-	milli gram per liter	$mg\ L^{-1}$
Cl^-	milli gram per liter	$mg\ L^{-1}$
Na^+	milli gram per liter	$mg\ L^{-1}$
K^+	milli gram per liter	$mg\ L^{-1}$
Ca^{2+}	milli gram per liter	$mg\ L^{-1}$
Mg^{2+}	milli gram per liter	$mg\ L^{-1}$
NH_4^+	milli gram per liter	$mg\ L^{-1}$

The participating laboratories were informed that concentration of each parameter was prepared within the range described in Table 5.3.

Table 5.3 Concentration range of artificial inland water sample

Parameter	Range	Parameter	Range
pH	5.0 – 8.0	Na^+	1 – 10 $mg\ L^{-1}$
EC	1.5 – 15 $mS\ m^{-1}$	K^+	0.2 – 2 $mg\ L^{-1}$
Alkalinity	0.05 – 0.5 $meq\ L^{-1}$	Ca^{2+}	0.5 – 5 $mg\ L^{-1}$
SO_4^{2-}	2 – 20 $mg\ L^{-1}$	Mg^{2+}	0.2 – 2 $mg\ L^{-1}$
NO_3^-	0.1 – 5 $mg\ L^{-1}$	NH_4^+	0.05 – 0.5 $mg\ L^{-1}$
Cl^-	1 – 10 $mg\ L^{-1}$		

5.2.3 Parameters analyzed

Participating laboratories are required to apply the analytical methods and data checking procedures specified in the technical documents in EANET to the analysis. The methods and procedures applied were specified in Technical Manual for Inland Aquatic Environment Monitoring in East Asia (2010).

Analytical methods specified in the manual are described in Table 5.4.

Table 5.4 Analytical methods specified in the Technical Manual

Parameter	Analytical method
pH	Glass electrode
EC	Conductivity cell
Alkalinity	Titration by Burette or Digital Burette with pH Meter (end-point pH 4.8)
SO_4^{2-} NO_3^-	Ion Chromatography or Spectrophotometry
Cl^-	Ion Chromatography or Titration
Na^+ K^+ Ca^{2+} Mg^{2+}	Ion Chromatography or Atomic Absorption / Flame (emission) photometry
NH_4^+	Ion Chromatography or Spectrophotometry (Indophenol blue)

5.2.4 Data Checking Procedures

a) Calculation of ion balance (*R_1*)

(1) Total anion equivalent concentration (A [μeq L^{-1}]) was calculated by summing the concentrations of all anions (c [μmol L^{-1}]) and alkalinity (*ALK*: μeq L^{-1}). Alkalinity was considered to be corresponded to bicarbonate ions (HCO_3^-).

$$\mathbf{A}\ [\mu eq\ L^{-1}] = \sum n\ c_{Ai}\ [\mu mol\ L^{-1}] = 2c\ (SO_4^{2-}) + c\ (NO_3^-) + c\ (Cl^-) + (ALK)$$

n, c_{Ai} : electric charge and concentration [μmol L^{-1}] of anion “i”.

(2) Total cation equivalent concentration (**C** [μeq L^{-1}]) was calculated by summing the concentrations of all cations (c [μmol L^{-1}]).

$$\mathbf{C}\ [\mu eq\ L^{-1}] = \sum n\ c_{Ci}\ [\mu mol\ L^{-1}] = 10^{(6-pH)} + c\ (NH_4^+) + c\ (Na^+) + c\ (K^+) + 2c\ (Ca^{2+}) + 2c\ (Mg^{2+})$$

n, c_{Ci} : electric charge and concentration [μmol L^{-1}] of cation “i”.

(3) Calculation of ion balance (R_1)

$$R_1 = 100 \times (\boldsymbol{C}-\boldsymbol{A}) / (\boldsymbol{C}+\boldsymbol{A})\ [\%]$$

(4) R_1, which is calculated using the above equation, should be compared with allowable ranges in Table 5.5. Re-measurement, check with standard solutions, and/or inspection of calibration

curves should be undertaken, when R_1 is not within the range.

Table 5.5 Allowable ranges for R_1 in different concentration ranges

$(C+A)$ [μeq L^{-1}]	R_1 [%]
< 50	+30 ~ −30
50 ~ 100	+15 ~ −15
>100	+8 ~ − 8

b) Comparison between calculated and measured electrical conductivity (R_2)

(1) Total electric conductivity (Λcalc) is calculated as follows;

$$\Lambda\text{calc (mS m}^{-1}) = \{349.7\times10^{(6-\text{pH})} + 80.0\times2C\,(\text{SO}_4^{2-}) + 71.4\times C\,(\text{NO}_3^-) + 76.3\times C\,(\text{Cl}^-) + 73.5\times C\,(\text{NH}_4^+) + 50.1\times C\,(\text{Na}^+) + 73.5\times C\,(\text{K}^+) + 59.8\times2C\,(\text{Ca}^{2+}) + 53.0\times2C\,(\text{Mg}^{2+}) + 44.5\times(ALK)\}/10000$$

C: Molar concentrations [μmol L^{-1}] of ions in the parenthesis; each constant value was ionic equivalent conductance at 25 degrees centigrade. Alkalinity was considered to be corresponded to bicarbonate ions (HCO_3^-).

(2) Ratio (R_2) of calculations (Λcalc) to measurements (Λmeas) in electric conductivity is calculated as follows;

$$R_2 = 100\times(\Lambda\text{calc}-\Lambda\text{meas})/(\Lambda\text{calc}+\Lambda\text{meas})\ [\%]$$

Λ meas : measured conductivity

(3) R_2, which is calculated using the above equation, is compared with allowable ranges in Table 5.6. Re-measurement, check with standard solutions, and/or inspection of calibration curves are necessary, when R_2 is not within the range.

Table 5.6 Allowable ranges for R_2 in different concentration ranges

Λmeas[mS m^{-1}]	R_2 [%]
< 0.5	+ 20 ~ −20
0.5 ~ 3	+13 ~ −13
> 3	+9 ~ −9

5.3 Results

5.3.1 Outline of Results

Table 5.7 shows the summary of the analytical results. The outliers, defined as those results exceeding three standard deviations, were excluded from calculations in Table 5.7. Each average of submitted data agreed well with the corresponding prepared value/concentration. Original data from the laboratories are shown in Table 5.10 and APPENDIX table 5.1.

Table 5.7 Summary of analytical results of the artificial inland aquatic environment sample
(Reported data after outliers were removed)

Constituents	Prepared	Average	S.D.	N	Min.	Max.
pH	7.06	6.72	0.42	16	5.63	7.14
EC (mS m^{-1})	3.03	2.95	0.07	16	2.84	3.09
Alkalinity (meq L^{-1})	0.119	0.124	0.01	16	0.112	0.132
SO_4^{2-} (mg L^{-1})	3.83	3.86	0.10	17	3.64	4.05
NO_3^- (mg L^{-1})	0.55	0.59	0.07	16	0.50	0.74
Cl^- (mg L^{-1})	1.75	1.78	0.13	16	1.56	2.18
Na^+ (mg L^{-1})	2.74	2.69	0.17	16	2.12	2.87
K^+ (mg L^{-1})	0.52	0.52	0.04	16	0.47	0.63
Ca^{2+} (mg L^{-1})	1.29	1.45	0.10	15	1.30	1.64
Mg^{2+} (mg L^{-1})	0.53	0.54	0.06	16	0.38	0.62
NH_4^+ (mg L^{-1})	0.27	0.24	0.04	16	0.20	0.35

(note) Prepared: value calculated from the amount of chemicals used for the preparation of samples.
S.D.: standard deviation, N: number of data, Min: the minimum data, Max: the maximum data

The Data Quality Objectives (DQOs) of the EANET are specified in Chapter 6 of the Technical Manual. In this report, analytical data were compared with the prepared values/concentrations and evaluated by the criteria : A flag E is given to the value in the case that its deviation exceeds ±15% but not ±30%, and the flag X is given to the value in the case that its deviation exceeds ±30%.

Table 5.8 shows the number of flagged data for each parameter and Figure 5.1 shows the percentage of flagged data.

Table 5.8 Number of flagged data

Flag*	pH	EC	Alkalinity	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	Total	Ratio
E	2	0	0	0	1	1	1	1	7	2	6	21	11.7%
X	0	0	0	0	2	1	0	0	0	0	0	3	1.7%
Data within DQOs	14	16	16	17	14	15	15	15	9	14	10	155	86.6%
Flagged(%)	12.5	0.0	0.0	0.0	17.6	11.8	6.3	6.3	43.8	12.5	37.5	13.4	

Flag E: 15% < |Deviation| ≦ 30%
Flag X: 30% < |Deviation|

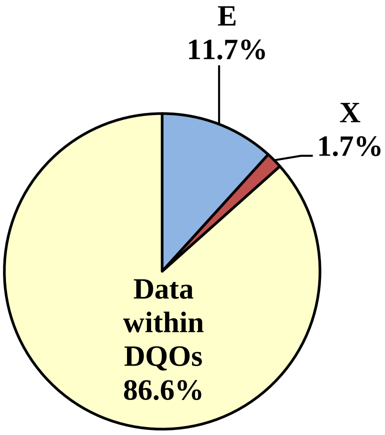


Figure 5.1 Percentage of flagged data

The data flagged by "E" shared 11.7% of all reported data, and the data flagged by "X" shared 1.7% of all reported data of samples. The Ca^{2+} results were flagged most (E and X), and their percentage was 43.8%.

The distribution of flagged data in each laboratory is shown in Table 5.9 and Figure 5.2.

Table 5.9 Number of flagged data in each laboratory

Number of flagged data	Number of laboratories	Ratio
0	5	29%
1	6	35%
2	4	24%
3	0	0%
4	1	6%
5	0	0%
6	1	6%
7	0	0%
8	0	0%
9	0	0%
Total	17	100%

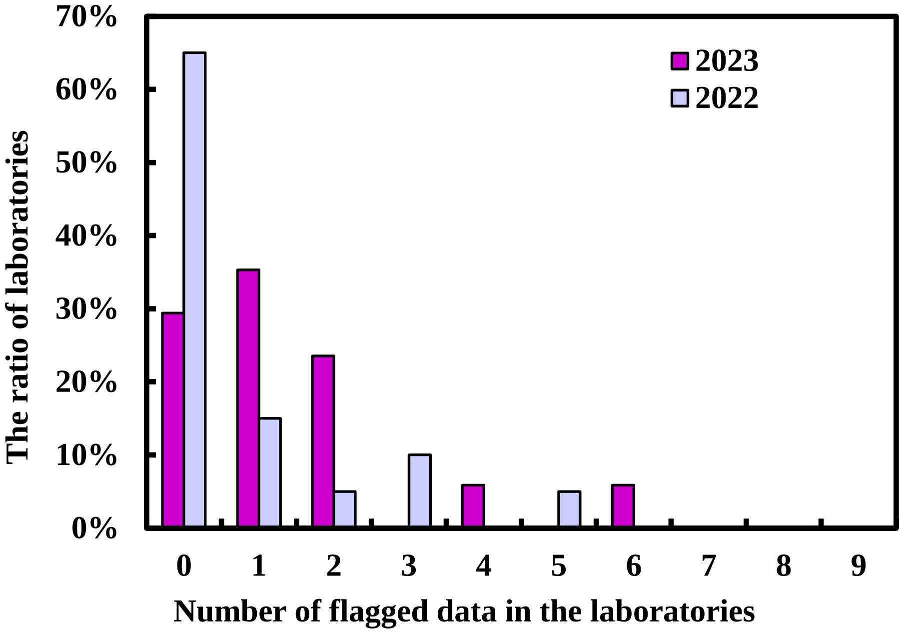


Figure 5.2 Distribution of laboratories with the number of flagged data

The percentage of the laboratories without flagged data was 29% in this attempt, while that in the last attempt (2022) was 65%. The maximum number of flagged data was six, which was submitted by one laboratory.

The Analytical data submitted by the participating laboratories are shown in Table 5.10 with flags.

Table 5.10 Analytical Results of Sample No.231i (artificial inland aquatic environment sample : EANET in 2023)

Lab. ID	pH	EC	Alkalinity	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	R1	R2
	-	mS m^{-1}	meq L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	%	%
CN01	7.00	3.09	0.124	3.91	0.57	1.76	2.77	0.52	1.50 E	0.49	0.23	-0.47	0.30
CN02	6.98	3.06	0.122	3.92	0.57	1.72	2.75	0.53	1.50 E	0.49	0.23	-0.03	0.49
CN03	6.99	2.95	0.125	3.89	0.57	1.71	2.71	0.51	1.50 E	0.49	0.23	-0.86	2.22
CN04	6.98	3.05	0.132	3.84	0.55	1.75	2.71	0.51	1.51 E	0.50	0.23	-1.87	1.14
JP03	6.93	2.94	0.123	3.86	0.53	1.70	2.76	0.51	1.48	0.55	0.24	1.09	2.64
JP04	7.04	2.93	0.126	3.82	0.54	1.75	2.70	0.53	1.30	0.54	0.23	-2.03	1.93
LA01				3.67	0.49	1.56	2.72	0.52	1.39	0.54	0.34 E		
MY01	7.14	2.90	0.120	3.80	0.54	1.73	2.74	0.51	1.32	0.53	0.35 E	0.87	2.78
MN01	6.40	2.92	0.112	4.05	0.62	1.89	2.87	0.49	1.55 E	0.60	0.20 E	2.97	4.41
PH01	6.99	2.85	0.131	3.75	0.72 X	1.72	2.63	0.63 E	1.30	0.58	0.23	-2.41	4.03
TH01	6.88	2.84	0.127	3.64	0.50	1.71							
TH02	5.92 E	2.86	0.125	3.94	0.54	1.77	2.79	0.49	0.95 E	0.38 E	0.21 E	-8.20 I	1.27
VN01	6.70	2.99	0.122	3.90	0.63	1.86	2.74	0.49	1.43	0.59	0.25	-0.03	2.59
VN02	6.68	3.01	0.117	3.90	0.58	1.81	2.76	0.52	1.42	0.56	0.26	1.20	1.61
VN03	5.63 E	2.95	0.130	3.93	0.65 E	6.12 X	2.12 E	0.57	1.64 E	0.59	0.21 E	-22.26 I	16.43 C
VN04	6.75	2.97	0.126	3.89	0.74 X	1.90	2.71	0.47	1.45	0.62 E	0.26	-0.87	3.70
VN05	6.59	2.96	0.129	3.92	0.61	2.18 E	2.53	0.56	1.48	0.55	0.21 E	-4.95	3.90
Expected value	7.06	3.03	0.119	3.83	0.55	1.75	2.74	0.52	1.29	0.53	0.27	-	-

Flag E: 15% < \|Deviation\| ≦ 30%

Flag X: 30% < \|Deviation\|

I: Poor ion balance (R1)

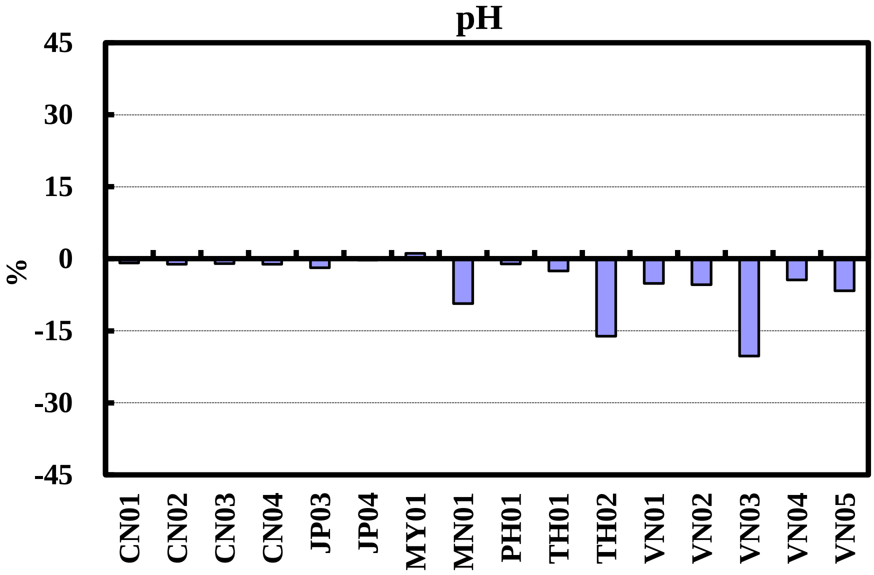
C: Rich Conductivity agreement (R2)

blank: not analyzed

5.3.2 Evaluation of laboratories' performance (by analytical parameters)

The laboratories' performances are presented below in Figures from 5.3 to 5.13 for each analytical parameter. The results received from each laboratory are normalized by the prepared values to evaluate deviation from the prepared values.

Figure 5.3 Distribution of results for pH (normalized by the prepared value)



Except for TH02 and VN03, all the submitted data of pH were within DQOs.

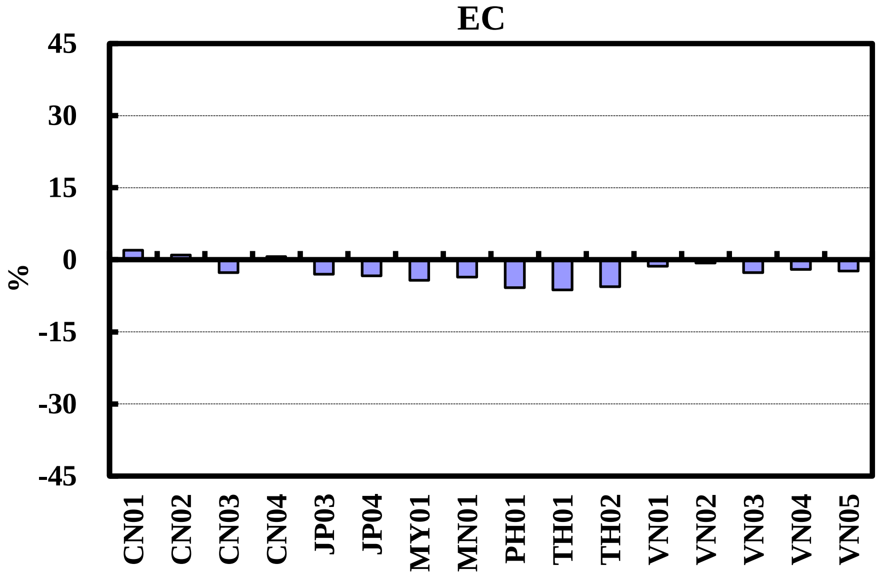


Figure 5.4 Distribution of results for EC (normalized by the prepared value)

All the submitted data of EC were within DQOs.

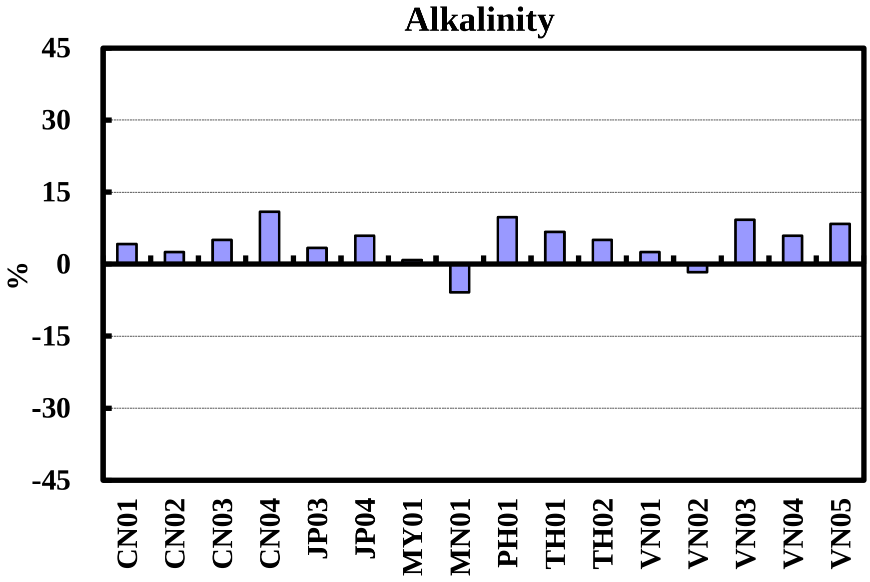


Figure 5.5 Distribution of results for alkalinity (normalized by prepared concentration)

All the submitted data of Alkalinity were within DQOs.

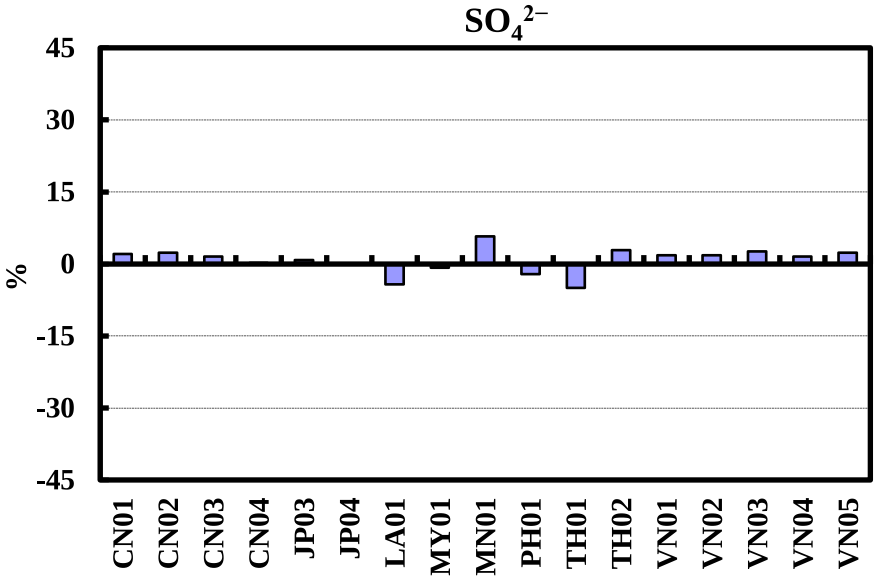


Figure 5.6 Distribution of results for SO_4^{2-} (normalized by prepared concentration)

All the submitted data of SO_4^{2-} were within DQOs.

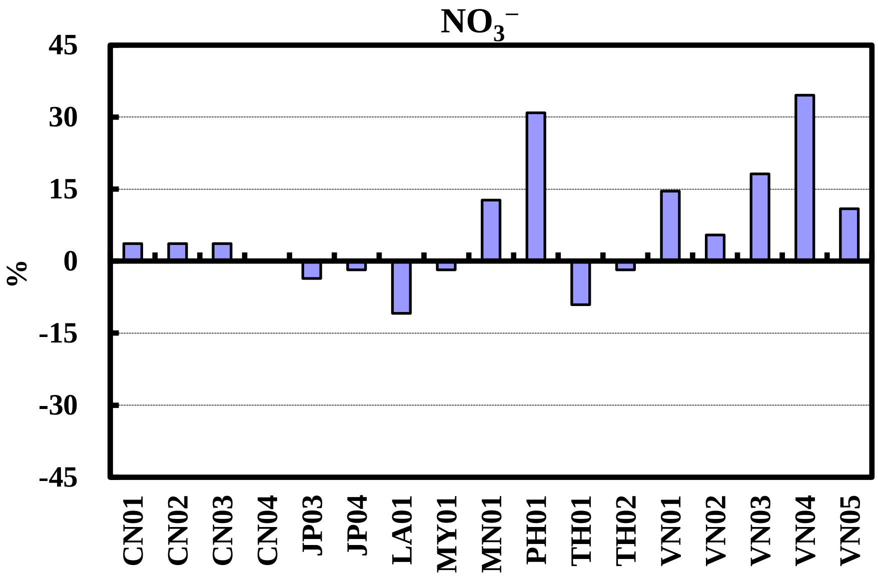


Figure 5.7 Distribution of results for NO_3^- (normalized by prepared concentration)

Except for PH01, VN03 and VN04, all the submitted data of NO_3^- were within DQOs.

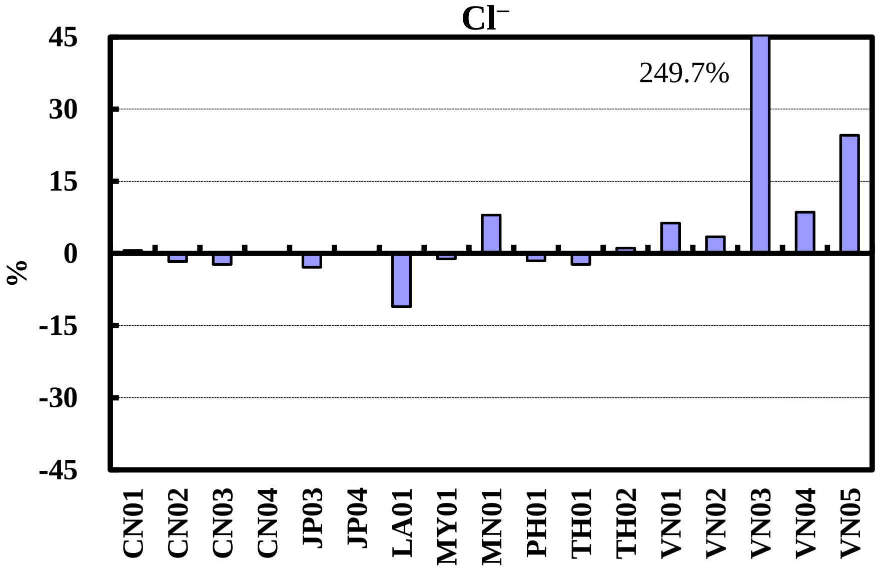


Figure 5.8 Distribution of results for Cl^- (normalized by prepared concentration)

Except for VN03 and VN05, all the submitted data of Cl^- were within DQOs.

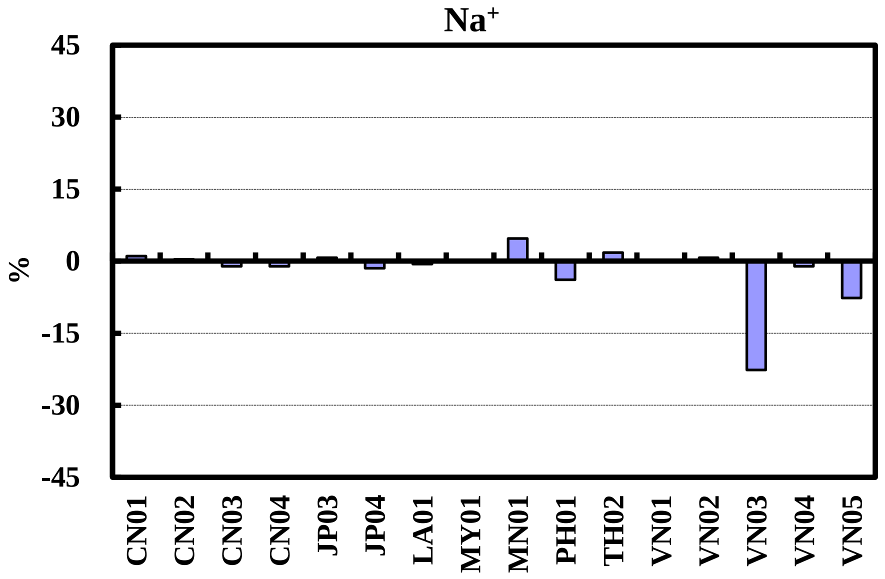


Figure 5.9 Distribution of results for Na$^+$ (normalized by prepared concentration)

Except for VN03, all the submitted data of Na$^+$ were within DQOs.

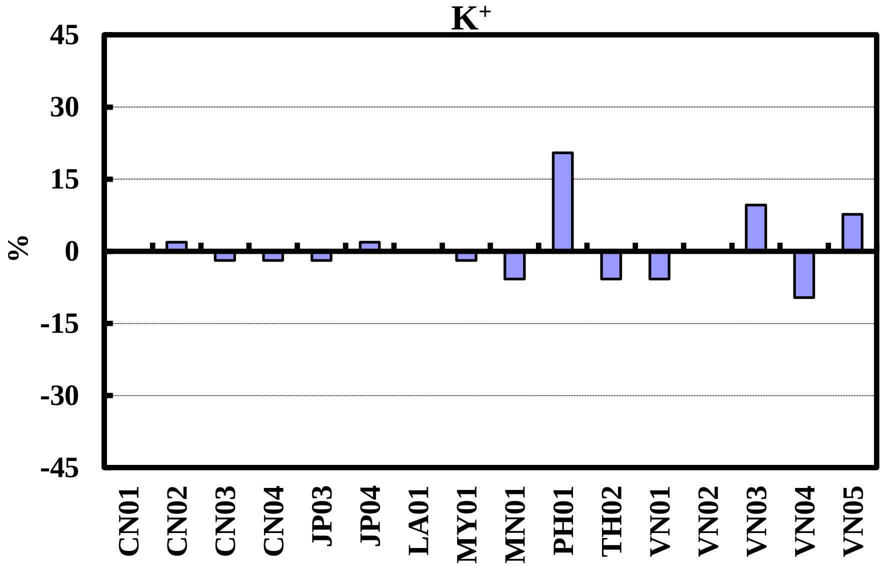


Figure 5.10 Distribution of results for K$^+$ (normalized by prepared concentration)

Except for PH01, all the submitted data of K$^+$ were within DQOs.

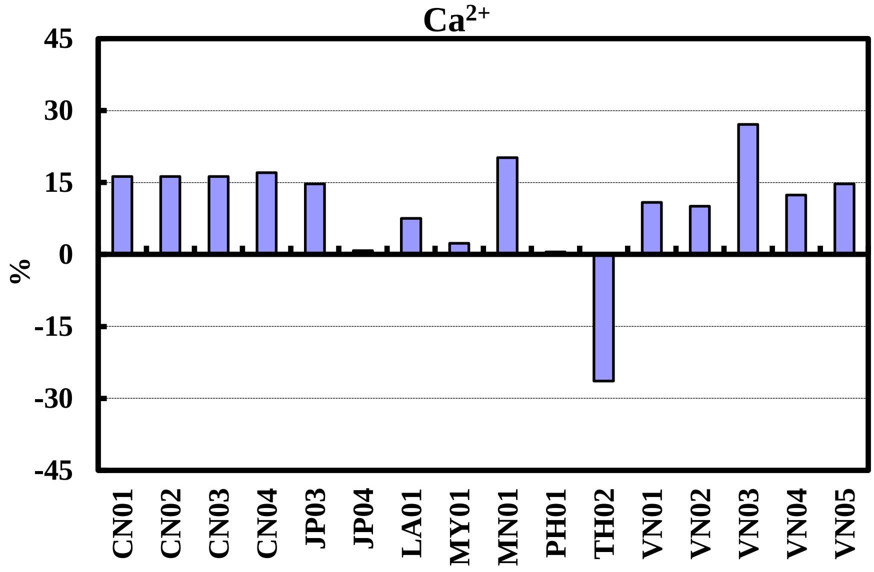


Figure 5.11 Distribution of results for Ca^{2+} (normalized by prepared concentration)

Data of Ca^{2+} from 7 laboratories were flagged. The number of flagged data of Ca^{2+} was 1 in the last attempt(2022).

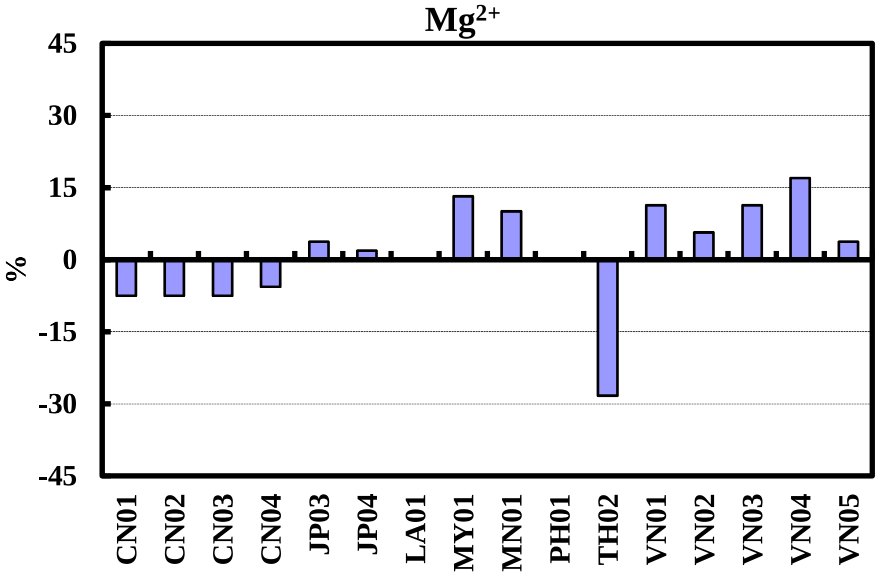


Figure 5.12 Distribution of results for Mg^{2+} (normalized by prepared concentration)

Except for TH02 and VN04, all the submitted data of Mg^{2+} were within DQOs.

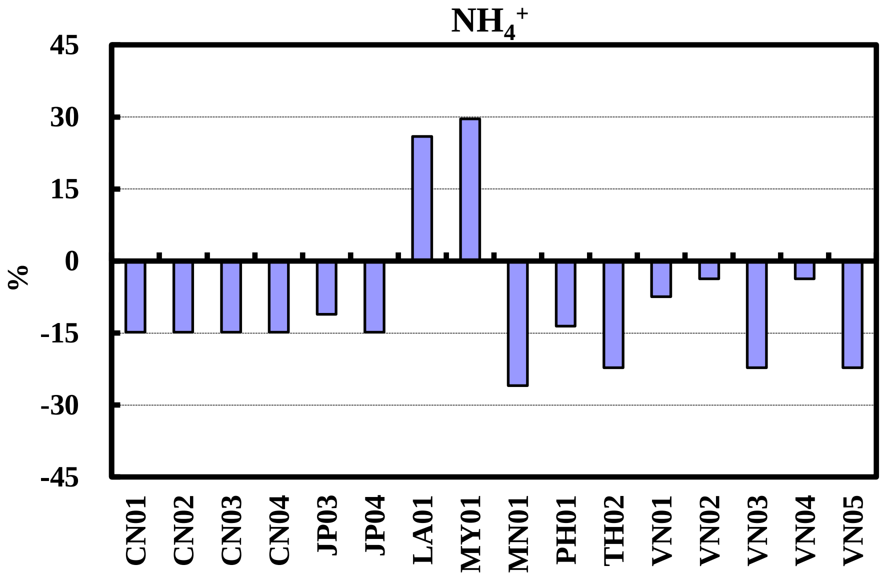


Figure 5.13 Distribution of results for NH_4^+ (normalized by prepared concentration)

Data of NH_4^+ from 6 laboratories were flagged. The number of flagged data of NH_4^+ was 4 in the last attempt (2022). Among 16 participating laboratories, 14 laboratories used ion chromatography, 2 laboratories used spectrophotometry (Indophenol) for the determination of NH_4^+. 5 laboratories with flagged data used ion chromatography, and another 1 laboratory used spectrophotometry (Indophenol) method.

5.3.3 Overall Evaluation

Calculated relative standard deviation of the whole sets of analytical data is presented in Figure 5.14 with comparison to last attempt (2022).

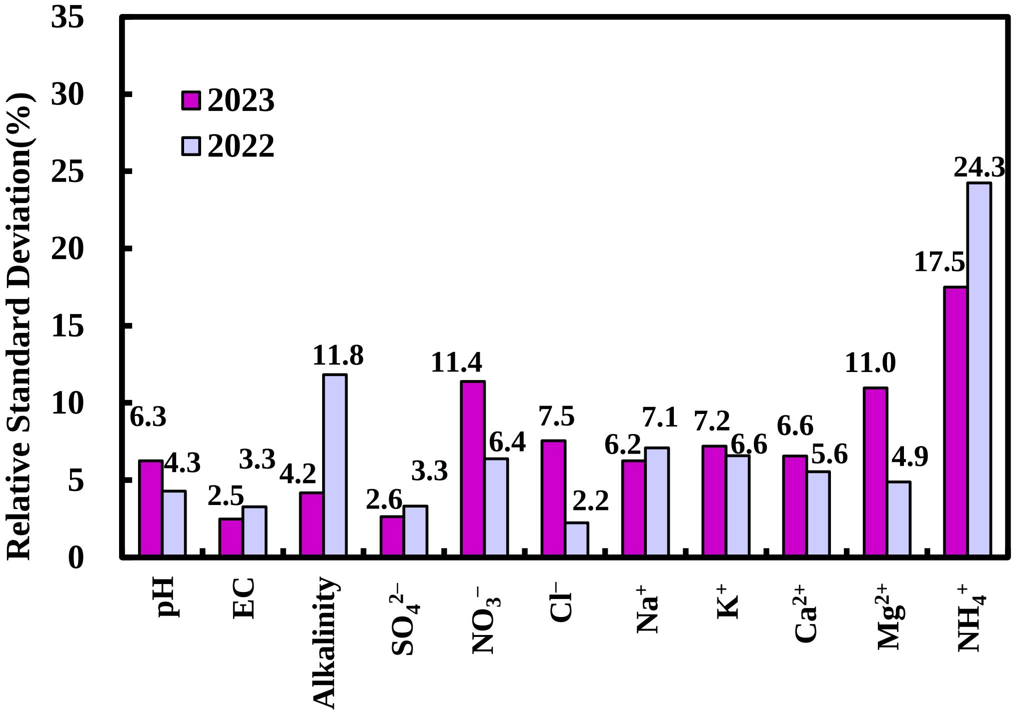


Figure 5.14 Relative standard deviation of each constituent

(Relative standard deviation (%) = Standard deviation / Average × 100, Reported data after outliers were removed)

The relative standard deviation (RSD) of Alkalinity and NH_4^+ in 2023 were particularly lower than the last attempt (2022). On the other hand, the RSDs of NO_3^-, Cl^- and Mg^{2+} were particularly increased in this attempt.

5.3.4 Information on laboratories

Methodologies used

The percentages of laboratories using the recommended methods are shown in Figure 5.15, and the codes used for the various analytical methods are shown in Table 5.11 and 5.12.

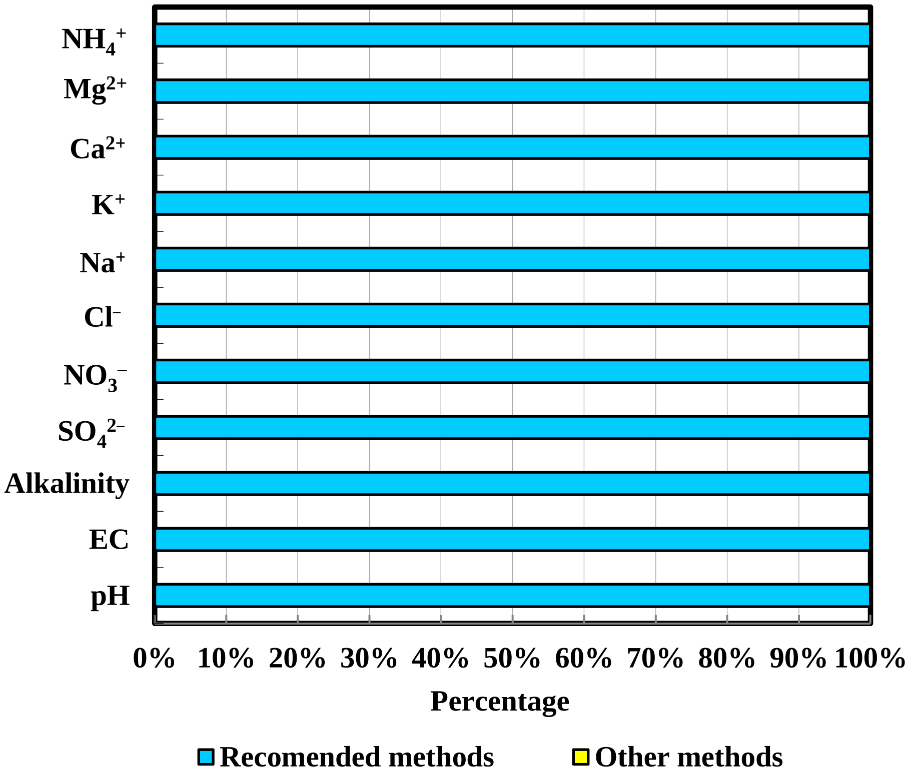


Figure 5.15 Percentage of laboratories using the recommended methods

Table 5.11 List of methods

Code	Method
0	pH meter with electrode
1	Conductivity cell
2	Titration
3	Atomic absorption / Flame (emission) photometry
4	Ion chromatography
5	Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP - AES)
6	Calculation
7	Spectrophotometry
8	Spectrophotometry (Indophenol blue)
9	Inductively Coupled Plasma - Mass Spectrometry (ICP - MS)
10	Other method

Table 5.12 Analytical methods

Code	pH	EC	Alkalinity	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
0	16(2)										
1		16									
2			16			1(1)					
3							2(1)	2(1)	2(1)	2	
4				16	16(2)	16(1)	14	14	14(6)	14(2)	14(5)
5											
6											
7				1	1(1)						
8											2(1)
9											
10											
Flagged E	2	0	0	0	1	1	1	1	7	2	6
Flagged X	0	0	0	0	2	1	0	0	0	0	0

▨ Recommended methods ☐ Other methods

( ) : Number of data, which flagged by "E" or "X"

The participating laboratories used recommended methods of the EANET.

For the determination of anions/cations, most of the participating laboratories used ion chromatography, while some of them used other methods. Either data of all anions/cations obtained through ion chromatography included some flagged data. As a conclusion, there was no clear relationship between analytical methods and appearance of flagged data.

<u>Staff (numbers and years of experience)</u>

Number of staff in charge of measurement in each laboratory is shown in Table 5.13.

Table 5.13 Staff in charge of measurement

Lab.ID	Total	pH	EC	Alkalinity	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
CN01	2	A	A	A	B	B	B	B	B	B	B	B
CN02	2	A	A	A	B	B	B	B	B	B	B	B
CN03	2	A	A	A	B	B	B	B	B	B	B	B
CN04	1	A	A	A	A	A	A	A	A	A	A	A
JP03	2	A	A	B	B	B	B	B	B	B	B	B
JP04	1	A	A	A	A	A	A	A	A	A	A	A
LA01	1				A	A	A	A	A	A	A	A
MY01	4	A	A	B	C	C	C	D	D	D	D	D
MN01	2	A	A	A	B	B	B	B	B	B	B	B
PH01	4	A	A	A	B	B	B	C	C	C	C	D
TH01	1	A	A	A	A	A	A					
TH02	2	A,B	A,B	A,B	A,B	A,B	A,B	A,B	A,B	A,B	A,B	A,B
VN01	2	A	A	A	B	B	B	B	B	B	B	B
VN02	3	A	A	B	C	C	C	C	C	C	C	C
VN03	2	A	A	B	B	A	A	B	B	B	B	A
VN04	3	A	A	B	C	C	C	C	C	C	C	C
VN05	2	A	A	A	B	B	B	B	B	B	B	B

The letters of A,B,C···mean individuals of staff in each laboratory who are in charge of measurement.

▨ Reverse mesh: "E" or "X" in sample flagged Data.

blank: not analyzed

In many laboratories, 2 or 3 persons analyzed the sample, and usually they shared the works according to the methods such as pH, EC and ionic items.

There was no clear relationship between data quality and the number of staff in charge of measurement.

Years of experience of each laboratory are shown in Table 5.14.

Table 5.14 Years of experience

Unit : year

Lab.ID	pH	EC	Alkalinity	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
CN01	5	5	5	6	6	6	6	6	6	6	6
CN02	5	5	5	9	9	9	9	9	9	9	9
CN03	11	11	11	25	25	25	25	25	25	25	25
CN04	17	17	17	17	17	17	17	17	17	17	17
JP03	4	4	20	20	20	20	20	20	20	20	20
JP04	21	21	21	21	21	21	21	21	21	21	21
LA01				12	12	12	12	12	12	12	12
MY01	10	10	9	11	11	11	1	1	1	1	1
MN01	22	22	22	25	25	25	25	25	25	25	25
PH01	9	9	9	4	4	4	4	4	4	4	13
TH01	25	25	25	25	25	25					
TH02	25	25	25	25	25	25	25	25	25	25	25
VN01	7	7	7	10	10	10	10	10	10	10	10
VN02	17	17	19	19	19	19	19	19	19	19	19
VN03	9	9	12	12	9	9	12	12	12	12	9
VN04	20	20	19	20	20	20	20	20	20	20	20
VN05	18	18	18	19	19	19	19	19	19	19	19

▨ Data were Flagged by “E” or “X” in sample

1 year means experienced with one year or less.

blank: not analyzed

There was no clear relationship between data quality and years of experience.

5.4. Comparison with past surveys

The inter-laboratory comparison projects of the EANET have been carried out 23 times, and the results showing the percentage of flagged data and the percentage of data that satisfied the DQOs are shown in Figure 5.16.

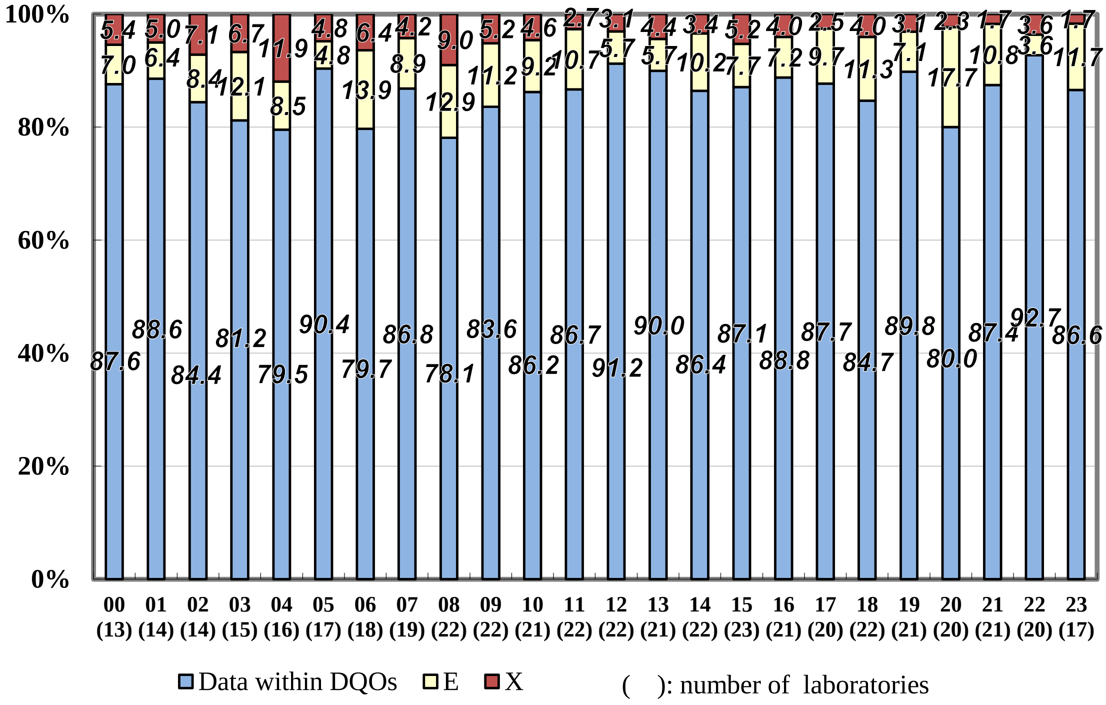


Figure 5.16 Comparison of the results from the inter-laboratory comparison projects

The percentage of data satisfied the DQOs decreased from the last attempt (2022).

The values/concentrations for each parameter from the 1st to 24th projects were compared with the percentage of flagged data in Figure 5.17.

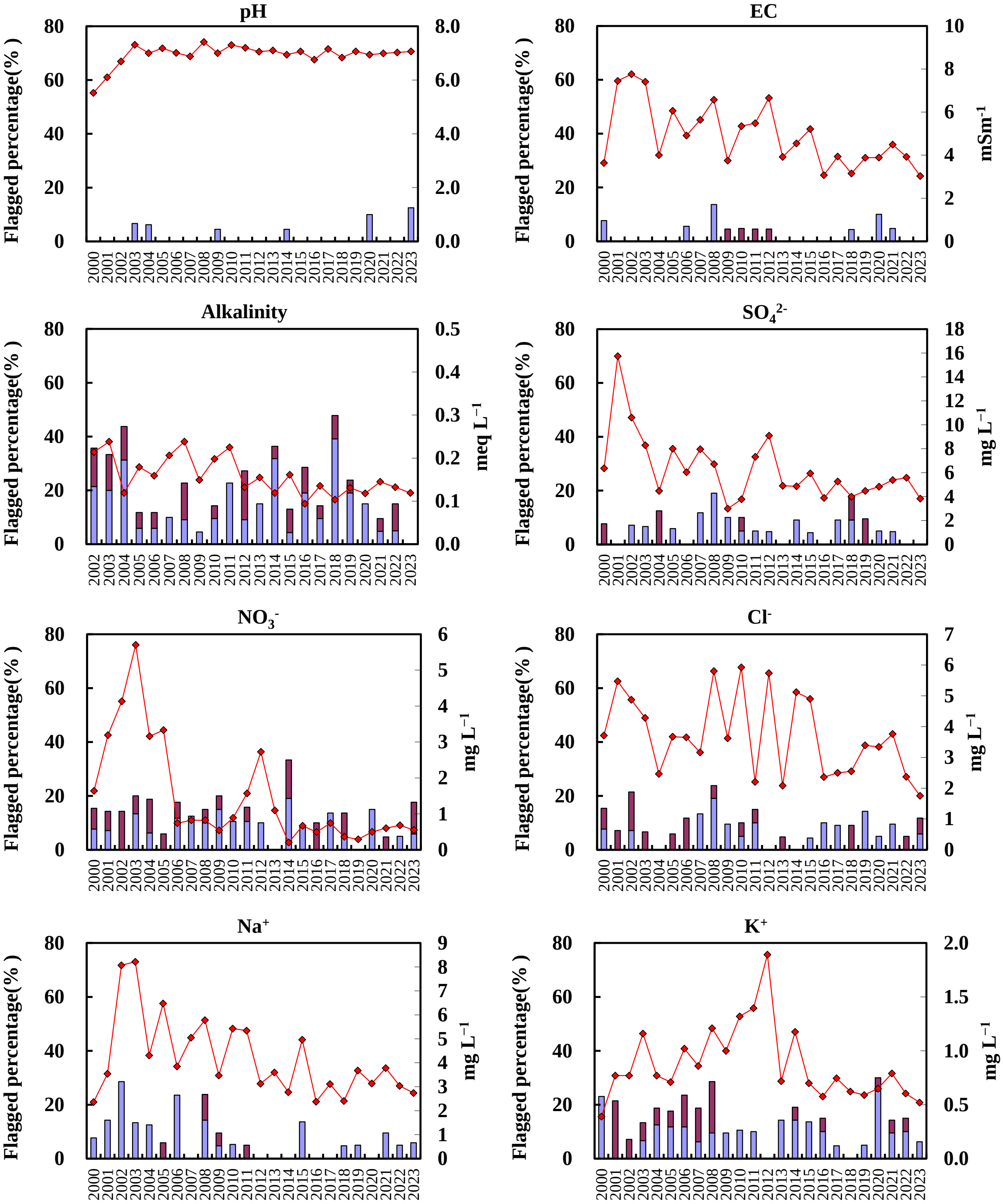


Figure 5.17 Concentrations and the percentage of flagged data for each parameter in inter-laboratory comparison projects

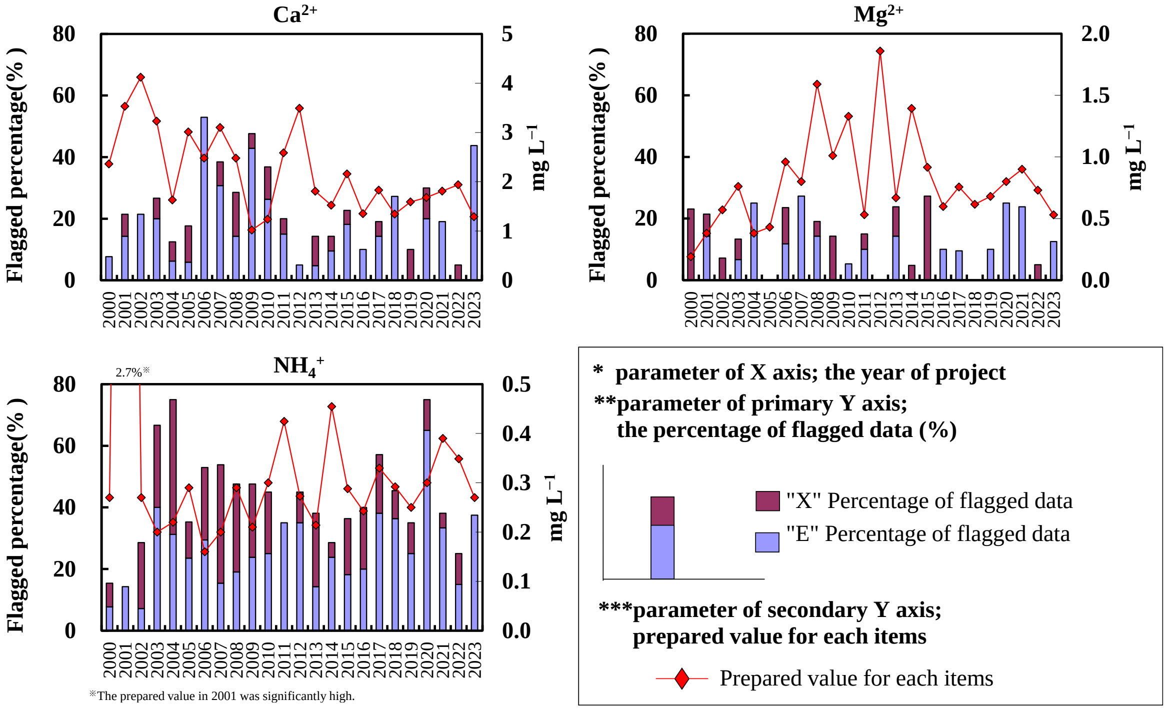


Figure 5.17 Concentrations and the percentage of flagged data for each parameter in inter-laboratory comparison projects (Continued)

There was no flagged data in EC, Alkalinity and SO_4^{2-} in this attempt. The analysis of K^+ was improved. In this attempt, flagged percentages of pH, NO_3^-, Cl^-, Na^+, Ca^{2+}, Mg^{2+} and NH_4^+ became higher than the last attempt.

Furthermore, the percentage of flagged data was larger in NH_4^+ than for other parameters in every survey except for the 1st- 2nd project. Therefore, in the inland water analysis, it is necessary to pay more attention to NH_4^+.

5.5. Recommendations for improvement

The following fundamental matters should be taken into account in measurement, analysis, and data control processes for improvement of precision.

5.5.1 Measurement and Analysis

1) General

- ►Clearance from contamination of the apparatus, materials and reagents used for measurement and analysis must be confirmed beforehand.
- ►Blank values of target substances should be as low as possible.
- ►Measurement and analysis should be conducted by persons who are well trained.
- ►To maintain high analytical quality, SOP (Standard Operating Procedures) must be prepared for the management of apparatus, reagents, and procedure of operation.

2) Deionized water

- ►Water with conductivity less than 0.15 mS m^{-1} is acceptable for measurements, analyses, dilution of precipitation samples and cleaning.

3) Certified materials and certified samples

- ►The measurements are evaluated by comparison of measured results of samples and certified materials.
- ►In order to assure the reliability of measurements, the certified solutions and materials should be used as much as possible.

4) Pretreatment of samples at analytical laboratory

- ►Conductivity and pH should be measured as soon as possible after sample receiving, and checking agreement of samples and sample list.
- ►Effort should be made to start analysis of the other parameters within a week of sample arrival in the laboratory and to complete the data sets by measuring EC, pH and all other chemical parameters.

5) Calibration of analytical instruments

- ►Each of the analytical instruments must be calibrated when they are used, and they should be adjusted as appropriate.

5.5.2 Evaluation of reliability

1) Sensitivity fluctuation of analytical instruments

When numerous samples are measured, measurements should only be continued after confirming that the sensitivity fluctuation is within the prescribed range.

For example, in ion chromatography

- ►A new calibration should be performed before the measurements are reached to over 30 samples.
- ►Reference materials should be measured after the calibration. It should also be done once or twice before the next calibration.
- ►Control charts should be applied for the measurement of the reference materials.
- ►Standard solutions and reference solutions must be prepared from different stock solutions in order to be independent.
- ►If the results of the control solutions are outside of 3 standard deviations, or out of 15% from the expected value, the reasons should be found and corrections should be made, and reference solution should be measured again.
- ►If the retention time changes slowly while the separator column is deteriorating, then adequate actions should be taken as appropriate. If it changes significantly in a relatively short time, the reasons should be found and removed, then the reference material must be measured again.

5.5.3 Data control

1) Data checks by the analytical laboratories

- ►When the sensitivity of instruments is not stable, when the results of duplicate analyses or re-measurements are significantly different, or when the percentage of a theoretical value to that for determined data in ion balances and electrical conductivity is significantly different from 1.0, measurement should be repeated since reliability is low.
- ►When samples seem to be obviously contaminated, these data should be treated as unrecorded data.
- ►Abnormal or unrecorded data can corrupt research results. So, careful checks are needed to avoid data of questionable quality. When abnormal or unrecorded data is detected, the process should be carefully reviewed to prevent the occurrence of the same problem in the future.

References

EANET (2000). *Technical Manual for Monitoring on Inland Aquatic Environment in East Asia.* Acid Deposition and Oxidant Research Center, Niigata, Japan, 46p.

EANET (2000). *Quality Assurance/Quality Control (QA/QC) Program for Monitoring on Inland Aquatic Environment in East Asia.* Acid Deposition and Oxidant Research Center, Niigata, Japan, 22p.

EANET (2010). *Technical Manual for Inland Aquatic Environment Monitoring in East Asia* -*2010.* Asia Center for Air Pollution Research, Niigata, Japan, 124.

Appendix Table 5.1 Results submitted by the laboratories

	pH	EC	Alkalinity	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
Lab. ID	-	(mS m^{-1})	(meq L^{-1})	(mg L^{-1})	(mg L^{-1})	(mg L^{-1})	(mg L^{-1})	(mg L^{-1})	(mg L^{-1})	(mg L^{-1})	(mg L^{-1})
CN01	7.00	3.09	0.124	3.91	0.57	1.76	2.77	0.52	1.50	0.49	0.23
CN02	6.98	3.06	0.122	3.92	0.57	1.72	2.75	0.53	1.50	0.49	0.23
CN03	6.99	2.95	0.125	3.89	0.57	1.71	2.71	0.51	1.50	0.49	0.23
CN04	6.98	3.05	0.132	3.84	0.55	1.75	2.71	0.51	1.51	0.50	0.23
JP03	6.93	2.94	0.123	3.86	0.53	1.70	2.76	0.51	1.48	0.55	0.24
JP04	7.04	2.93	0.126	3.82	0.54	1.75	2.70	0.53	1.30	0.54	0.23
LA01				3.67	0.49	1.56	2.72	0.52	1.39	0.54	0.34
MY01	7.14	2.90	0.120	3.80	0.54	1.73	2.74	0.51	1.32	0.53	0.35
MN01	6.40	2.92	0.112	4.05	0.62	1.89	2.87	0.49	1.55	0.60	0.20
PH01	6.99	2.85	0.131	3.75	0.72	1.72	2.63	0.63	1.30	0.58	0.23
TH01	6.88	2.84	0.127	3.64	0.50	1.71					
TH02	5.92	2.86	0.125	3.94	0.54	1.77	2.79	0.49	0.95	0.38	0.21
VN01	6.70	2.99	0.122	3.90	0.63	1.86	2.74	0.49	1.43	0.59	0.25
VN02	6.68	3.01	0.117	3.90	0.58	1.81	2.76	0.52	1.42	0.56	0.26
VN03	5.63	2.95	0.130	3.93	0.65	6.12	2.12	0.57	1.64	0.59	0.21
VN04	6.75	2.97	0.126	3.89	0.74	1.90	2.71	0.47	1.45	0.62	0.26
VN05	6.59	2.96	0.129	3.92	0.61	2.18	2.53	0.56	1.48	0.55	0.21
Expected value	7.06	3.03	0.119	3.83	0.55	1.75	2.74	0.52	1.29	0.53	0.27
Number of data	16	16	16	17	17	17	16	16	16	16	16
Average	6.72	2.95	0.12	3.86	0.59	2.04	2.69	0.52	1.42	0.54	0.24
Minimum	5.63	2.84	0.11	3.64	0.49	1.56	2.12	0.47	0.95	0.38	0.20
Maximum	7.14	3.09	0.13	4.05	0.74	6.12	2.87	0.63	1.64	0.62	0.35

blank: not analyzed

Appendix Table 5.2 Data normalized by the prepared value

(Original data / Expected Value − 1) ×100 (%)

Lab. ID	pH (%)	EC (%)	Alkalinity (%)	SO_4^{2-} (%)	NO_3^- (%)	Cl^- (%)	Na^+ (%)	K^+ (%)	Ca^{2+} (%)	Mg^{2+} (%)	NH_4^+ (%)
CN01	-0.8	2.0	4.2	2.1	3.6	0.6	1.1	0.0	16.3	-7.5	-14.8
CN02	-1.1	1.0	2.5	2.3	3.6	-1.7	0.4	1.9	16.3	-7.5	-14.8
CN03	-1.0	-2.6	5.0	1.6	3.6	-2.3	-1.1	-1.9	16.3	-7.5	-14.8
CN04	-1.1	0.7	10.9	0.3	0.0	0.0	-1.1	-1.9	17.1	-5.7	-14.8
JP03	-1.8	-3.0	3.4	0.8	-3.6	-2.9	0.7	-1.9	14.7	3.8	-11.1
JP04	-0.3	-3.3	5.9	-0.3	-1.8	0.0	-1.5	1.9	0.8	1.9	-14.8
LA01				-4.3	-10.9	-11.0	-0.6	0.0	7.5	1.9	25.9
MY01	1.1	-4.3	0.8	-0.8	-1.8	-1.1	0.0	-1.9	2.3	0.0	29.6
MN01	-9.3	-3.6	-5.9	5.7	12.7	8.0	4.7	-5.8	20.2	13.2	-25.9
PH01	-1.0	-5.8	9.8	-2.1	30.9	-1.5	-3.9	20.5	0.5	10.1	-13.6
TH01	-2.5	-6.3	6.7	-5.0	-9.1	-2.3					
TH02	-16.1	-5.6	5.0	2.9	-1.8	1.1	1.8	-5.8	-26.4	-28.3	-22.2
VN01	-5.1	-1.3	2.5	1.8	14.5	6.3	0.0	-5.8	10.9	11.3	-7.4
VN02	-5.4	-0.7	-1.7	1.8	5.5	3.4	0.7	0.0	10.1	5.7	-3.7
VN03	-20.3	-2.6	9.2	2.6	18.2	249.7	-22.6	9.6	27.1	11.3	-22.2
VN04	-4.4	-2.0	5.9	1.6	34.5	8.6	-1.1	-9.6	12.4	17.0	-3.7
VN05	-6.7	-2.3	8.4	2.3	10.9	24.6	-7.7	7.7	14.7	3.8	-22.2
Minimum	-20.3	-6.3	-5.9	-5.0	-10.9	-11.0	-22.6	-9.6	-26.4	-28.3	-25.9
Maximum	1.1	2.0	10.9	5.7	34.5	249.7	4.7	20.5	27.1	17.0	29.6
Average	-4.7	-2.5	4.6	0.8	6.4	16.4	-1.9	0.4	10.0	1.5	-9.4

blank: not analyzed

6. ACKNOWLEDGEMENT

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7. CONTACT INFORMATION

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